



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> METHOD OF TREATING A TEXTILE  <b>(57) Abstract</b> <p>A method of treating a textile such as a laundry fabric is provided, in which the textile is contacted with an organic substance which forms a complex with a transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment. The organic substance may be used in dry form, or in a liquor that is then dried, such as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. The method can confer cleaning benefits to the textile after the treatment. Also provided is a dry textile having an organic substance applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.</p>		

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## METHOD OF TREATING A TEXTILE

This invention relates to a method of treating textiles such as laundry fabrics, more  
5 specifically to a method whereby bleaching by atmospheric oxygen is catalysed after the  
treatment. This invention also relates to textiles thus treated.

In a conventional bleaching treatment, a substrate such as a laundry fabric or other  
textile is contacted is subjected to hydrogen peroxide, or to substances which can  
10 generate hydroperoxyl radicals, such as inorganic or organic peroxides.

A preferred approach to generating hydroperoxyl bleach radicals is the use of inorganic  
peroxides coupled with organic precursor compounds. These systems are employed for  
many commercial laundry powders. For example, various European systems are based  
15 on tetraacetyl ethylenediamine (TAED) as the organic precursor coupled with sodium  
perborate or sodium percarbonate, whereas in the United States laundry bleach products  
are typically based on sodium nonanoyloxybenzenesulphonate (SNOBS) as the organic  
precursor coupled with sodium perborate. Alternatively, or additionally, hydrogen  
peroxide and peroxy systems can be activated by bleach catalysts, such as by complexes  
20 of iron and the ligand N4Py (*i.e.* N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-  
yl)methylamine) disclosed in WO95/34628, or the ligand Tpen (*i.e.* N, N, N', N'-  
tetra(pyridin-2-yl-methyl)ethylenediamine) disclosed in WO97/48787. It has long been  
thought desirable to be able to use atmospheric oxygen (air) as the source for a  
bleaching species, as this would avoid the need for costly hydroperoxyl generating  
25 systems. Unfortunately, air as such is kinetically inert towards bleaching substrates and  
exhibits no bleaching ability. Recently some progress has been made in this area. For  
example, WO 97/38074 reports the use of air for oxidising stains on fabrics by bubbling  
air through an aqueous solution containing an aldehyde and a radical initiator, whereas  
according to WO95/34628 and WO97/48787 referred to above, molecular oxygen may

be used as the oxidant with the iron catalysts, as an alternative to peroxide generating systems.

However, the known art teaches a bleaching effect only as long as the substrate is being  
5 subjected to the bleaching treatment. Thus, there is no expectation that hydrogen  
peroxide or peroxy bleach systems could continue to provide a bleaching effect on a  
treated substrate, such as a laundry fabric after washing and drying, since the bleaching  
species themselves or any activators necessary for the bleaching systems would be  
assumed to be removed from the substrate, or consumed or deactivated, on completing  
10 the wash cycle and drying.

It would be desirable to be able to treat a textile such that, after the treatment is  
completed, a bleaching effect is observed on the textile. Furthermore, it would be  
desirable to be able to provide a bleach treatment for textiles such as laundry fabrics  
15 whereby residual bleaching occurs when the treated fabric has been treated and is dry.

We have now found this can be achieved by a treatment method in accordance with the  
present invention, by catalysing bleaching of the substrate by atmospheric oxygen after  
treatment of the substrate.

20

Accordingly, the present invention provides a method of treating a textile by contacting  
the textile with an organic substance which forms a complex with a transition metal,  
whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the  
treatment.

25

The present invention further provides a dry textile having an organic substance as  
defined above applied or deposited thereon, whereby bleaching by atmospheric oxygen  
is catalysed on the textile.

Advantageously, by enabling a bleaching effect even after the textile has been treated, the benefits of bleaching can be prolonged on the textile. Furthermore, since a bleaching effect is conferred to the textile after the treatment, the treatment itself, such as a laundry wash cycle, may for example be shortened. Moreover, since a bleaching effect is achieved by atmospheric oxygen after treatment of the textile, hydrogen peroxide or peroxy-based bleach systems can be omitted from the treatment substance.

The organic substance may be contacted to the textile fabric in any suitable manner. For example, it may be applied in dry form, such as in powder form, or in a liquor that is then dried, for example as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. Other suitable means of contacting the organic substance to the textile may be used, as further explained below.

Any suitable textile that is susceptible to bleaching or one that one might wish to subject to bleaching may be used. Preferably the textile is a laundry fabric or garment.

In a preferred embodiment, the method according to the present invention is carried out on a laundry fabric using an aqueous treatment liquor. In particular, the treatment may be effected in a wash cycle for cleaning laundry. More preferably, the treatment is carried out in an aqueous detergent bleach wash liquid.

In a preferred embodiment, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated temperatures.

The bleaching method may be carried out by simply leaving the substrate in contact with the organic substance for a sufficient period of time. Preferably, however, the organic substance is in an aqueous medium, and the aqueous medium on or containing the substrate is agitated.

The organic substance can be contacted to the textile fabric in any conventional manner. For example it may be applied in dry form, such as in powder form, or in a liquor that is then dried, for example in an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid.

5

In a preferred embodiment, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated temperatures.

10 In a particularly preferred embodiment the method according to the present invention is carried out on a laundry fabric using aqueous treatment liquor. In particular the treatment may be effected in, or as an adjunct to, an essentially conventional wash cycle for cleaning laundry. More preferably, the treatment is carried out in an aqueous detergent wash liquor. The organic substance can be delivered into the wash liquor from a powder, granule, pellet, tablet, block, bar or other such solid form. The solid form can  
15 comprise a carrier, which can be particulate, sheet-like or comprise a three-dimensional object. The carrier can be dispersible or soluble in the wash liquor or may remain substantially intact. In other embodiments, the organic substance can be delivered into the wash liquor from a paste, gel or liquid concentrate.

20 It is particularly advantageous that the organic substance used in the method of the present invention makes use of atmospheric oxygen in its bleaching activity. This avoids the requirement that peroxygen bleaches and/or other relatively large quantities of reactive substances need be used in the treatment process. Consequently, only a relatively small quantity of bleach active substance need be employed and this allows  
25 dosage routes to be exploited which could previously not be used. Thus, while it is preferable to include the organic substance in a composition that is normally used in a washing process, such as a pre-treatment, main-wash, conditioning composition or ironing aid, other means for ensuring that the organic substance is present in the wash liquor may be envisaged.

30

For example, it is envisaged that the organic substance can be presented in the form of a body from which it is slowly released during the whole or part of the laundry process. Such release can occur over the course of a single wash or over the course of a plurality of washes. In the latter case it is envisaged that the organic substance can be released  
5 from a carrier substrate used in association with the wash process, e.g. from a body placed in the dispenser drawer of a washing machine, elsewhere in the delivery system or in the drum of the washing machine. When used in the drum of the washing machine the carrier can be freely moving or fixed relative to the drum. Such fixing can be achieved by mechanical means, for example by barbs that interact with the drum wall, or  
10 employ other forces, for example a magnetic force. The modification of a washing machine to provide for means to hold and retain such a carrier is envisaged similar means being known from the analogous art of toilet block manufacture. Freely moving carriers such as shuttles for dosage of surfactant materials and/or other detergent ingredients into the wash can comprise means for the release of the organic substance  
15 into the wash.

In the alternative, the organic substance can be presented in the form of a wash additive that preferably is soluble. The additive can take any of the physical forms used for wash additives, including powder, granule, pellet, sheet, tablet, block, bar or other such solid  
20 form or take the form of a paste, gel or liquid. Dosage of the additive can be unitary or in a quantity determined by the user. While it is envisaged that such additives can be used in the main washing cycle, the use of them in the conditioning or drying cycle is not hereby excluded.

25 The present invention is not limited to those circumstances in which a washing machine is employed, but can be applied where washing is performed in some alternative vessel. In these circumstances it is envisaged that the organic substance can be delivered by means of slow release from the bowl, bucket or other vessel which is being employed, or from any implement which is being employed, such as a brush, bat or dolly, or from  
30 any suitable applicator.

Suitable pre-treatment means for application of the organic substance to the textile material prior to the main wash include sprays, pens, roller-ball devices, bars, soft solid applicator sticks and impregnated cloths or cloths containing microcapsules. Such means are well known in the analogous art of deodorant application and/or in spot treatment of textiles. Similar means for application are employed in those embodiments where the organic substance is applied after the main washing and/or conditioning steps have been performed, e.g. prior to or after ironing or drying of the cloth. For example, the organic substance may be applied using tapes, sheets or sticking plasters coated or impregnated with the substance, or containing microcapsules of the substance. The organic substance may for example be incorporated into a drier sheet so as to be activated or released during a tumble-drier cycle, or the substance can be provided in an impregnated or microcapsule-containing sheet so as to be delivered to the textile when ironed.

The organic substance may comprise a preformed complex of a ligand and a transition metal. Alternatively, the organic substance may comprise a free ligand that complexes with a transition metal already present in the water or that complexes with a transition metal present in the substrate. The organic substance may also be included in the form of a composition of a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal, whereby the complex is formed *in situ* in the medium.

The organic substance forms a complex with one or more transition metals, in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron I-IV, copper I-III, cobalt I-III, nickel I-III, chromium II-VII, silver I-II, titanium II-IV, tungsten IV-VI, palladium II, ruthenium II-V, vanadium II-V and molybdenum II-VI.

In a preferred embodiment, the organic substance forms a complex of the general formula (A1):



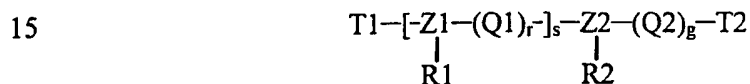


in which:

- 5 M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(I)-(II)-(III)-(IV), Co(I)-(II)-(III), Ni(I)-(II)-(III), Cr(II)-(III)-(IV)-(V)-(VI)-(VII), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI), W(IV)-(V)-(VI), Pd(II), Ru(II)-(III)-(IV)-(V) and Ag(I)-(II), and preferably selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II), Fe(II)-(III)-(IV) and Co(I)-(II)-(III);
- 10 L represents a ligand as herein defined, or its protonated or deprotonated analogue;
- X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner, preferably selected from  $O^{2-}$ ,  $RBO_2^{2-}$ ,  $RCOO^-$ ,  $RCONR^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $NO$ ,  $CO$ ,  $S^{2-}$ ,  $RS^-$ ,  $PO_3^{4-}$ , STP-derived anions,  $PO_3OR^{3-}$ ,  $H_2O$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $ROH$ ,  $NRR'R''$ ,  $RCN$ ,  $Cl^-$ ,  $Br^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $CN^-$ ,  $N_3^-$ ,  $F^-$ ,  $I^-$ ,  $RO^-$ ,  $ClO_4^-$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$  and  $RSO_3^-$ , and more preferably selected from  $O^{2-}$ ,  $RBO_2^{2-}$ ,  $RCOO^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $NO$ ,  $CO$ ,  $CN^-$ ,  $S^{2-}$ ,  $RS^-$ ,  $PO_3^{4-}$ ,  $H_2O$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $ROH$ ,  $NRR'R''$ ,  $Cl^-$ ,  $Br^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $RCN$ ,  $N_3^-$ ,  $F^-$ ,  $I^-$ ,  $RO^-$ ,  $ClO_4^-$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$  and  $RSO_3^-$  (preferably  $CF_3SO_3^-$ );
- 20 Y represents any non-coordinated counter ion, preferably selected from  $ClO_4^-$ ,  $BR_4^-$ ,  $[FeCl_4]^-$ ,  $PF_6^-$ ,  $RCOO^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $RO^-$ ,  $N^+RR'R''R'''$ ,  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $I^-$ ,  $RSO_3^-$ ,  $S_2O_6^{2-}$ ,  $OCN^-$ ,  $SCN^-$ ,  $Li^+$ ,  $Ba^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Cs^+$ ,  $PR_4^+$ ,  $RBO_2^{2-}$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$ ,  $SbCl_6^-$ ,  $CuCl_4^{2-}$ ,  $CN$ ,  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ , STP-derived anions,  $CO_3^{2-}$ ,  $HCO_3^-$  and  $BF_4^-$ , and more preferably selected from  $ClO_4^-$ ,  $BR_4^-$ ,  $[FeCl_4]^-$ ,  $PF_6^-$ ,  $RCOO^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $RO^-$ ,  $N^+RR'R''R'''$ ,  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $I^-$ ,  $RSO_3^-$  (preferably  $CF_3SO_3^-$ ),  $S_2O_6^{2-}$ ,  $OCN^-$ ,  $SCN^-$ ,  $Li^+$ ,  $Ba^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $PR_4^+$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$ , and  $BF_4^-$ ;
- 25 R, R', R'', R''' independently represent a group selected from hydrogen, hydroxyl, -OR (wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or carbonyl derivative group), -OAr, alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups, each of R, Ar, alkyl, alkenyl, cycloalkyl,
- 30

- heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups being optionally substituted by one or more functional groups E, or R6 together with R7 and independently R8 together with R9 represent oxygen, wherein E is selected from functional groups containing oxygen, sulphur, phosphorus, nitrogen, selenium, halogens, and any electron donating and/or withdrawing groups, and preferably R, R', R'', R''' represent hydrogen, optionally substituted alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or C<sub>1-4</sub>-alkyl;
- a represents an integer from 1 to 10, preferably from 1 to 4;
- k represents an integer from 1 to 10;
- n represents zero or an integer from 1 to 10, preferably from 1 to 4;
- m represents zero or an integer from 1 to 20, preferably from 1 to 8.

Preferably, the ligand L is of the general formula (BI):

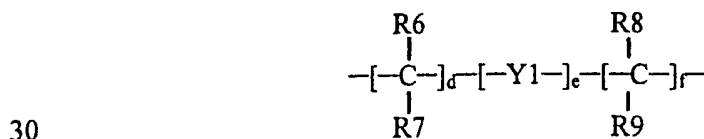


wherein

- g represents zero or an integer from 1 to 6;
- r represents an integer from 1 to 6;
- s represents zero or an integer from 1 to 6;

- Z1 and Z2 independently represent a heteroatom or a heterocyclic or heteroaromatic ring, Z1 and/or Z2 being optionally substituted by one or more functional groups E as defined below;

Q1 and Q2 independently represent a group of the formula:



wherein

$10 > d + e + f > 1$ ;  $d = 0-9$ ;  $e = 0-9$ ;  $f = 0-9$ ;

each Y1 is independently selected from -O-, -S-, -SO-, -SO<sub>2</sub>-, -(G<sup>1</sup>)N-, -  
 5 (G<sup>1</sup>)(G<sup>2</sup>)N- (wherein G<sup>1</sup> and G<sup>2</sup> are as defined below), -C(O)-, arylene, alkylene,  
 heteroarylene, -P- and -P(O)-;

if  $s > 1$ , each -[Z1(R1)-(Q1)<sub>r</sub>]- group is independently defined;

10 R1, R2, R6, R7, R8, R9 independently represent a group selected from  
 hydrogen, hydroxyl, -OR (wherein R = alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl,  
 heteroaryl or carbonyl derivative group), -OAr, alkyl, alkenyl, cycloalkyl,  
 heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups, each of R, Ar, alkyl,  
 alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups  
 15 being optionally substituted by one or more functional groups E, or R6 together with R7  
 and independently R8 together with R9 represent oxygen;

E is selected from functional groups containing oxygen, sulphur, phosphorus,  
 nitrogen, selenium, halogens, and any electron donating and/or withdrawing groups  
 (preferably E is selected from hydroxy, mono- or polycarboxylate derivatives, aryl,  
 20 heteroaryl, sulphonate, thiol (-RSH), thioethers (-R-S-R'), disulphides (-RSSR'),  
 dithiolenes, mono- or polyphosphonates, mono- or polyphosphates, electron donating  
 groups and electron withdrawing groups, and groups of formulae (G<sup>1</sup>)(G<sup>2</sup>)N-, (G<sup>1</sup>)(G<sup>2</sup>)  
 (G<sup>3</sup>)N-, (G<sup>1</sup>)(G<sup>2</sup>)N-C(O)-, G<sup>3</sup>O- and G<sup>3</sup>C(O)-, wherein each of G<sup>1</sup>, G<sup>2</sup> and G<sup>3</sup> is  
 independently selected from hydrogen, alkyl, electron donating groups and electron  
 25 withdrawing groups (in addition to any amongst the foregoing));

or one of R1-R9 is a bridging group bound to another moiety of the same general  
 formula;

T1 and T2 independently represent groups R4 and R5, wherein R4 and R5 are as  
 30 defined for R1-R9, and if  $g = 0$  and  $s > 0$ , R1 together with R4, and/or R2 together with

R5, may optionally independently represent =CH-R10, wherein R10 is as defined for R1-R9, or

T1 and T2 may together (-T2-T1-) represent a covalent bond linkage when  $s > 1$  and  $g > 0$ ;

5

if Z1 and/or Z2 represent N and T1 and T2 together represent a single bond linkage and R1 and/or R2 are absent, Q1 and/or Q2 may independently represent a group of the formula:  $=CH-[-Y1-]_e-CH=$ ,

10 optionally any two or more of R1, R2, R6, R7, R8, R9 independently are linked together by a covalent bond;

if Z1 and/or Z2 represents O, then R1 and/or R2 do not exist;

if Z1 and/or Z2 represents S, N, P, B or Si then R1 and/or R2 may be absent;

15 if Z1 and/or Z2 represents a heteroatom substituted by a functional group E then R1 and/or R2 and/or R4 and/or R5 may be absent.

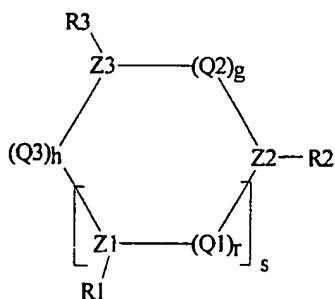
The groups Z1 and Z2 preferably independently represent an optionally substituted heteroatom selected from N, P, O, S, B and Si or an optionally substituted heterocyclic  
 20 ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidines, pyrazine, pyrimidine, pyrazole, pyrrole, imidazole, benzimidazole, quinoline, isoquinoline, carbazole, indole, isoindole, furane, thiophene, oxazole and thiazole.

25 The groups R1-R9 are preferably independently selected from -H, hydroxy-C<sub>0</sub>-C<sub>20</sub>-alkyl, halo-C<sub>0</sub>-C<sub>20</sub>-alkyl, nitroso, formyl-C<sub>0</sub>-C<sub>20</sub>-alkyl, carboxyl-C<sub>0</sub>-C<sub>20</sub>-alkyl and esters and salts thereof, carbamoyl-C<sub>0</sub>-C<sub>20</sub>-alkyl, sulpho-C<sub>0</sub>-C<sub>20</sub>-alkyl and esters and salts thereof, sulphamoyl-C<sub>0</sub>-C<sub>20</sub>-alkyl, amino-C<sub>0</sub>-C<sub>20</sub>-alkyl, aryl-C<sub>0</sub>-C<sub>20</sub>-alkyl, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyl, C<sub>0</sub>-C<sub>20</sub>-alkyl, alkoxy-C<sub>0</sub>-C<sub>8</sub>-alkyl, carbonyl-C<sub>0</sub>-C<sub>6</sub>-alkoxy, and aryl-C<sub>0</sub>-C<sub>6</sub>-alkyl  
 30 and C<sub>0</sub>-C<sub>20</sub>-alkylamide.

One of R1-R9 may be a bridging group which links the ligand moiety to a second ligand moiety of preferably the same general structure. In this case the bridging group may have the formula  $-C_{n'}(R11)(R12)-(D)_p-C_m(R11)(R12)-$  bound between the two moieties, wherein p is zero or one, D is selected from a heteroatom or a heteroatom-containing group, or is part of an aromatic or saturated homonuclear and heteronuclear ring, n' is an integer from 1 to 4, m' is an integer from 1 to 4, with the proviso that  $n'+m' \leq 4$ , R11 and R12 are each independently preferably selected from -H, NR13 and OR14, alkyl, aryl, optionally substituted, and R13 and R14 are each independently selected from -H, alkyl, aryl, both optionally substituted. Alternatively, or additionally, two or more of R1-R9 together represent a bridging group linking atoms, preferably hetero atoms, in the same moiety, with the bridging group preferably being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge.

15

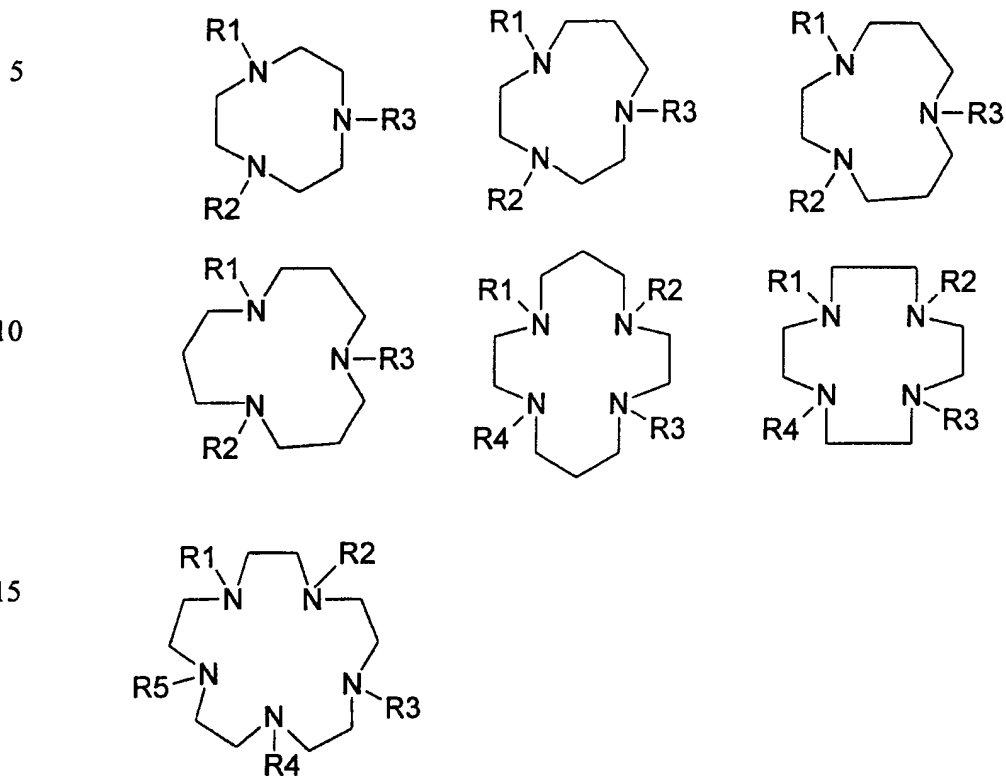
In a first variant according to formula (BI), the groups T1 and T2 together form a single bond linkage and  $s > 1$ , according to general formula (BII):



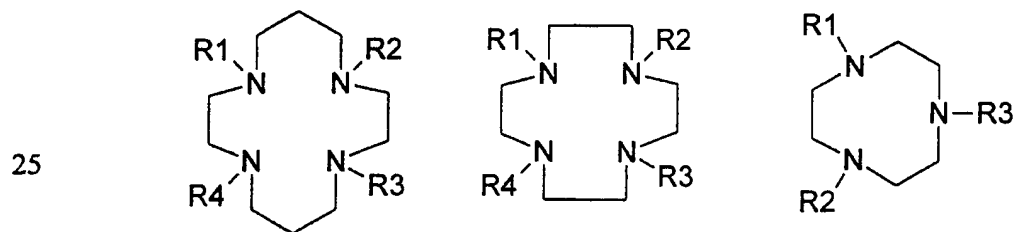
20

wherein Z3 independently represents a group as defined for Z1 or Z2; R3 independently represents a group as defined for R1-R9; Q3 independently represents a group as defined for Q1, Q2; h represents zero or an integer from 1 to 6; and  $s' = s - 1$ .

In a first embodiment of the first variant, in general formula (BII),  $s'=1, 2$  or  $3$ ;  
 $r=g=h=1$ ;  $d=2$  or  $3$ ;  $e=f=0$ ;  $R_6=R_7=H$ , preferably such that the ligand has a general  
 formula selected from:



20 and more preferably selected from:



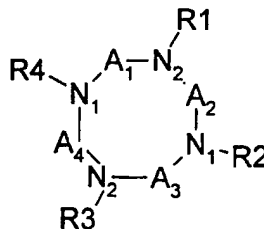
In these preferred examples,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are preferably independently selected  
 from  $-H$ , alkyl, aryl, heteroaryl, and/or one of  $R_1$ - $R_4$  represents a bridging group bound  
 30 to another moiety of the same general formula and/or two or more of  $R_1$ - $R_4$  together

represent a bridging group linking N atoms in the same moiety, with the bridging group being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge, preferably heteroarylene. More preferably, R1, R2, R3 and R4 are independently selected from -H, methyl, ethyl, isopropyl, nitrogen-containing heteroaryl, or a bridging group bound to  
 5 another moiety of the same general formula or linking N atoms in the same moiety with the bridging group being alkylene or hydroxy-alkylene.

According to this first embodiment, in the complex  $[M_a L_k X_n] Y_m$  preferably:

- M= Mn(II)-(IV), Cu(I)-(III), Fe(II)-(III), Co(II)-(III);  
 10 X= CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>, RCOO<sup>-</sup>;  
 Y= ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>  
 a= 1, 2, 3, 4;  
 n= 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;  
 15 m= 1, 2, 3, 4; and  
 k= 1, 2, 4.

In a second embodiment of the first variant, in general formula (BII), s'=2; r=g=h=1; d=f=0; e=1; and each Y1 is independently alkylene or heteroarylene. The ligand  
 20 preferably has the general formula:



wherein

- 25 A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub> are independently selected from C<sub>1-9</sub>-alkylene or heteroarylene groups; and  
 N<sub>1</sub> and N<sub>2</sub> independently represent a hetero atom or a heteroarylene group.

In a preferred second embodiment, N<sub>1</sub> represents an aliphatic nitrogen, N<sub>2</sub> represents a heteroarylene group, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> each independently represent -H, alkyl, aryl or heteroaryl, and A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, A<sub>4</sub> each represent -CH<sub>2</sub>-.

5

One of R<sub>1</sub>-R<sub>4</sub> may represent a bridging group bound to another moiety of the same general formula and/or two or more of R<sub>1</sub>-R<sub>4</sub> may together represent a bridging group linking N atoms in the same moiety, with the bridging group being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge. Preferably, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are  
 10 independently selected from -H, methyl, ethyl, isopropyl, nitrogen-containing heteroaryl, or a bridging group bound to another moiety of the same general formula or linking N atoms in the same moiety with the bridging group being alkylene or hydroxy-alkylene.

Particularly preferably, the ligand has the general formula:

15



20

wherein R<sub>1</sub>, R<sub>2</sub> each independently represent -H, alkyl, aryl or heteroaryl.

25 According to this second embodiment, in the complex [M<sub>a</sub>L<sub>k</sub>X<sub>n</sub>]Y<sub>m</sub> preferably:

M= Fe(II)-(III), Mn(II)-(IV), Cu(II), Co(II)-(III);

X= CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>,

RCOO<sup>-</sup>;

Y= ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>;

30

a= 1, 2, 3, 4;

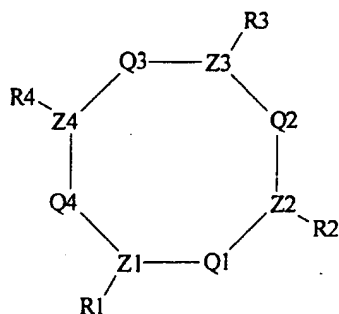
n= 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;



$m = 1, 2, 3, 4$ ; and

$k = 1, 2, 4$ .

- In a third embodiment of the first variant, in general formula (BII),  $s'=2$  and  $r=g=h=1$ ,  
 5 according to the general formula:

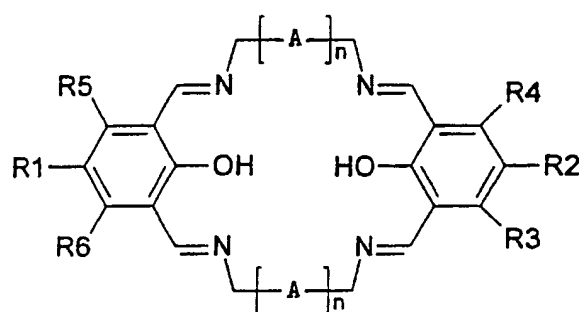


- In this third embodiment, preferably each Z1-Z4 represents a heteroaromatic ring;  
 10  $e=f=0$ ;  $d=1$ ; and R7 is absent, with preferably  $R1=R2=R3=R4=$  2,4,6-trimethyl-3-SO<sub>3</sub>Na-phenyl, 2,6-diCl-3(or 4)-SO<sub>3</sub>Na-phenyl.

Alternatively, each Z1-Z4 represents N; R1-R4 are absent; both Q1 and Q3 represent  $=CH-[-Y1-]_e-CH=$ ; and both Q2 and Q4 represent  $-CH_2-[-Y1-]_n-CH_2-$ .

15

Thus, preferably the ligand has the general formula:



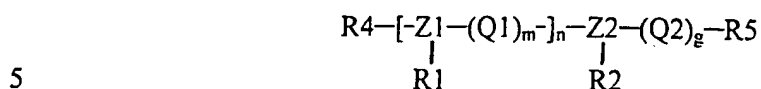
wherein A represents optionally substituted alkylene optionally interrupted by a heteroatom; and n is zero or an integer from 1 to 5.

- 5 Preferably, R1-R6 represent hydrogen, n=1 and A = -CH<sub>2</sub>-, -CHOH-, -CH<sub>2</sub>N(R)CH<sub>2</sub>- or -CH<sub>2</sub>CH<sub>2</sub>N(R)CH<sub>2</sub>CH<sub>2</sub>- wherein R represents hydrogen or alkyl, more preferably A = -CH<sub>2</sub>-, -CHOH- or -CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>-.

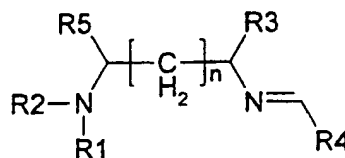
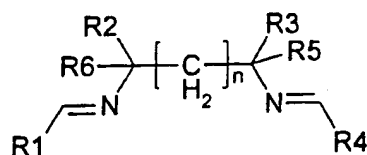
According to this third embodiment, in the complex [M<sub>a</sub>L<sub>k</sub>X<sub>n</sub>]Y<sub>m</sub> preferably:

- 10 M = Mn(II)-(IV), Co(II)-(III), Fe(II)-(III);  
 X = CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>, RCOO<sup>-</sup>;  
 Y = ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>;  
 a = 1, 2, 3, 4;  
 15 n = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;  
 m = 1, 2, 3, 4; and  
 k = 1, 2, 4.

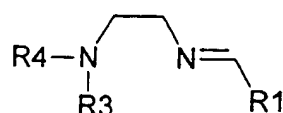
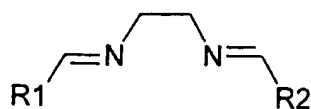
In a second variant according to formula (BI), T1 and T2 independently represent groups R4, R5 as defined for R1-R9, according to the general formula (BIII):



In a first embodiment of the second variant, in general formula (BIII),  $s=1$ ;  $r=1$ ;  $g=0$ ;  $d=f=1$ ;  $e=1-4$ ;  $Y1 = -CH_2-$ ; and R1 together with R4, and/or R2 together with R5, independently represent  $=CH-R10$ , wherein R10 is as defined for R1-R9. In one example, R2 together with R5 represents  $=CH-R10$ , with R1 and R4 being two separate groups. Alternatively, both R1 together with R4, and R2 together with R5 may independently represent  $=CH-R10$ . Thus, preferred ligands may for example have a



15 Preferably, the ligand is selected from:



wherein R1 and R2 are selected from optionally substituted phenols, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyls, alkylaryl, aminoalkyl, alkoxy, more preferably R1 and R2 being selected from optionally substituted phenols, heteroaryl-C<sub>0</sub>-C<sub>2</sub>-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, nitrogen-heteroaryl-C<sub>0</sub>-C<sub>2</sub>-alkyls.

According to this first embodiment, in the complex [M<sub>a</sub>L<sub>k</sub>X<sub>n</sub>]Y<sub>m</sub> preferably:

M= Mn(II)-(IV), Co(II)-(III), Fe(II)-(III);

10 X= CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>, RCOO<sup>-</sup>;

Y= ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>;

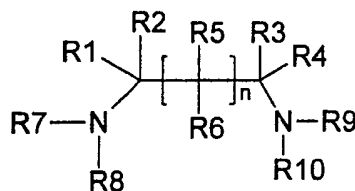
a= 1, 2, 3, 4;

n= 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;

15 m= 1, 2, 3, 4; and

k= 1, 2, 4.

In a second embodiment of the second variant, in general formula (BIII), s=1; r=1; g=0; d=f=1; e=1-4; Y1= -C(R')(R''), wherein R' and R'' are independently as defined for  
20 R1-R9. Preferably, the ligand has the general formula:



25

The groups R1, R2, R3, R4, R5 in this formula are preferably -H or C<sub>0</sub>-C<sub>20</sub>-alkyl, n=0 or 1, R6 is -H, alkyl, -OH or -SH, and R7, R8, R9, R10 are preferably each independently selected from -H, C<sub>0</sub>-C<sub>20</sub>-alkyl, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyl, alkoxy-C<sub>0</sub>-C<sub>8</sub>-alkyl and amino-C<sub>0</sub>-C<sub>20</sub>-alkyl.  
30

According to this second embodiment, in the complex  $[M_a L_k X_n] Y_m$  preferably:

$M = \text{Mn(II)-(IV)}, \text{Fe(II)-(III)}, \text{Cu(II)}, \text{Co(II)-(III)};$

$X = \text{CH}_3\text{CN}, \text{OH}_2, \text{Cl}^-, \text{Br}^-, \text{OCN}^-, \text{N}_3^-, \text{SCN}^-, \text{OH}^-, \text{O}^{2-}, \text{PO}_4^{3-}, \text{C}_6\text{H}_5\text{BO}_2^{2-},$

5  $\text{RCOO}^-;$

$Y = \text{ClO}_4^-, \text{BPh}_4^-, \text{Br}^-, \text{Cl}^-, [\text{FeCl}_4]^-, \text{PF}_6^-, \text{NO}_3^-;$

$a = 1, 2, 3, 4;$

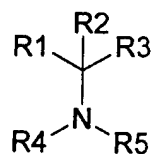
$n = 0, 1, 2, 3, 4;$

$m = 0, 1, 2, 3, 4, 5, 6, 7, 8;$  and

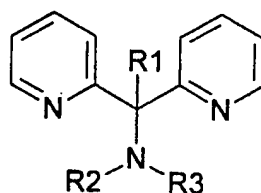
10  $k = 1, 2, 3, 4.$

In a third embodiment of the second variant, in general formula (BIII),  $s=0$ ;  $g=1$ ;  $d=e=0$ ;  $f=1-4$ . Preferably, the ligand has the general formula:

15



20 More preferably, the ligand has the general formula:



wherein R1, R2, R3 are as defined for R2, R4, R5.

25

According to this third embodiment, in the complex  $[M_a L_k X_n] Y_m$  preferably:

$M = \text{Mn(II)-(IV)}, \text{Fe(II)-(III)}, \text{Cu(II)}, \text{Co(II)-(III)};$

$X = \text{CH}_3\text{CN}, \text{OH}_2, \text{Cl}^-, \text{Br}^-, \text{OCN}^-, \text{N}_3^-, \text{SCN}^-, \text{OH}^-, \text{O}^{2-}, \text{PO}_4^{3-}, \text{C}_6\text{H}_5\text{BO}_2^{2-},$   
 $\text{RCOO}^-;$

$Y = \text{ClO}_4^-, \text{BPh}_4^-, \text{Br}^-, \text{Cl}^-, [\text{FeCl}_4]^-, \text{PF}_6^-, \text{NO}_3^-;$

$a = 1, 2, 3, 4;$

5  $n = 0, 1, 2, 3, 4;$

$m = 0, 1, 2, 3, 4, 5, 6, 7, 8;$  and

$k = 1, 2, 3, 4.$

10 In a fourth embodiment of the second variant, the organic substance forms a complex of the general formula (A):



in which

15 M represents iron in the II, III, IV or V oxidation state, manganese in the II, III, IV, VI or VII oxidation state, copper in the I, II or III oxidation state, cobalt in the II, III or IV oxidation state, or chromium in the II-VI oxidation state;

X represents a coordinating species;

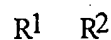
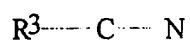
n represents zero or an integer in the range from 0 to 3;

20 z represents the charge of the complex and is an integer which can be positive, zero or negative;

Y represents a counter ion, the type of which is dependent on the charge of the complex;

$q = z/[\text{charge Y}];$  and

25 L represents a pentadentate ligand of the general formula (B):



wherein

each  $R^1$ ,  $R^2$  independently represents  $-R^4-R^5$ ,

$R^3$  represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or  $-R^4-R^5$ ,

5 each  $R^4$  independently represents a single bond or optionally substituted  
alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or  
carboxylic amide, and

each  $R^5$  independently represents an optionally N-substituted aminoalkyl group  
or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl,  
10 pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

The ligand L having the general formula (B), as defined above, is a pentadentate ligand.  
By 'pentadentate' herein is meant that five hetero atoms can coordinate to the metal M  
ion in the metal-complex.

15

In formula (B), one coordinating hetero atom is provided by the nitrogen atom in the  
methylamine backbone, and preferably one coordinating hetero atom is contained in  
each of the four  $R^1$  and  $R^2$  side groups. Preferably, all the coordinating hetero atoms are  
nitrogen atoms.

20

The ligand L of formula (B) preferably comprises at least two substituted or  
unsubstituted heteroaryl groups in the four side groups. The heteroaryl group is  
preferably a pyridin-2-yl group and, if substituted, preferably a methyl- or ethyl-  
substituted pyridin-2-yl group. More preferably, the heteroaryl group is an unsubstituted  
25 pyridin-2-yl group. Preferably, the heteroaryl group is linked to methylamine, and  
preferably to the N atom thereof, *via* a methylene group. Preferably, the ligand L of  
formula (B) contains at least one optionally substituted amino-alkyl side group, more  
preferably two amino-ethyl side groups, in particular 2-(N-alkyl)amino-ethyl or 2-(N,N-  
dialkyl)amino-ethyl.

30

Thus, in formula (B) preferably  $R^1$  represents pyridin-2-yl or  $R^2$  represents pyridin-2-yl-methyl. Preferably  $R^2$  or  $R^1$  represents 2-amino-ethyl, 2-(N-(m)ethyl)amino-ethyl or 2-(N,N-di(m)ethyl)amino-ethyl. If substituted,  $R^5$  preferably represents 3-methyl pyridin-2-yl.  $R^3$  preferably represents hydrogen, benzyl or methyl.

5

Examples of preferred ligands L of formula (B) in their simplest forms are:

(i) pyridin-2-yl containing ligands such as:

- N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine;
- 10 N,N-bis(pyrazol-1-yl-methyl)-bis(pyridin-2-yl)methylamine;
- N,N-bis(imidazol-2-yl-methyl)-bis(pyridin-2-yl)methylamine;
- N,N-bis(1,2,4-triazol-1-yl-methyl)-bis(pyridin-2-yl)methylamine;
- N,N-bis(pyridin-2-yl-methyl)-bis(pyrazol-1-yl)methylamine;
- N,N-bis(pyridin-2-yl-methyl)-bis(imidazol-2-yl)methylamine;
- 15 N,N-bis(pyridin-2-yl-methyl)-bis(1,2,4-triazol-1-yl)methylamine;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
- N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
- N,N-bis(pyrazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
- 20 N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
- N,N-bis(imidazol-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
- N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;
- N,N-bis(1,2,4-triazol-1-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-1-aminoethane;
- 25 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyrazol-1-yl)-2-phenyl-1-aminoethane;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-1-aminoethane;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(imidazol-2-yl)-2-phenyl-1-aminoethane;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(1,2,4-triazol-1-yl)-1-aminoethane;
- 30 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;



- N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane;  
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane;  
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(4-sulphonic acid-phenyl)-1-aminoethane;
- 5 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-2-yl)-1-aminoethane;  
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-3-yl)-1-aminoethane;  
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(pyridin-4-yl)-1-aminoethane;  
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-4-yl)-1-aminoethane;
- 10 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-3-yl)-1-aminoethane;  
 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-(1-alkyl-pyridinium-2-yl)-1-aminoethane;
- 15 (ii) 2-amino-ethyl containing ligands such as:  
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(pyridin-2-yl)methylamine;  
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(pyrazol-1-yl)methylamine;  
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(imidazol-2-yl)methylamine;  
 N,N-bis(2-(N-alkyl)amino-ethyl)-bis(1,2,4-triazol-1-yl)methylamine;
- 20 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(pyridin-2-yl)methylamine;  
 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(pyrazol-1-yl)methylamine;  
 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(imidazol-2-yl)methylamine;  
 N,N-bis(2-(N,N-dialkyl)amino-ethyl)-bis(1,2,4-triazol-1-yl)methylamine;  
 N,N-bis(pyridin-2-yl-methyl)-bis(2-amino-ethyl)methylamine;
- 25 N,N-bis(pyrazol-1-yl-methyl)-bis(2-amino-ethyl)methylamine;  
 N,N-bis(imidazol-2-yl-methyl)-bis(2-amino-ethyl)methylamine;  
 N,N-bis(1,2,4-triazol-1-yl-methyl)-bis(2-amino-ethyl)methylamine.

More preferred ligands are:

N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine, hereafter referred to as N4Py.

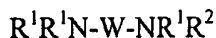
N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane, hereafter referred to as MeN4Py,

- 5 N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-2-phenyl-1-aminoethane, hereafter referred to as BzN4Py.

In an alternative fourth embodiment, the organic substance forms a complex of the general formula (A) including a ligand (B) as defined above, but with the proviso that  
10  $R^3$  does not represent hydrogen.

In a fifth embodiment of the second variant, the organic substance forms a complex of the general formula (A) as defined above, but wherein L represents a pentadentate or hexadentate ligand of general formula (C):

15



wherein

- each  $R^1$  independently represents  $-R^3-V$ , in which  $R^3$  represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and  
20 V represents an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;

- W represents an optionally substituted alkylene bridging group selected from  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ ,  $-CH_2-C_6H_4-CH_2-$ ,  $-CH_2-C_6H_{10}-CH_2-$ ,  
25 and  $-CH_2-C_{10}H_6-CH_2-$ ; and

- $R^2$  represents a group selected from  $R^1$ , and alkyl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and  $N^+(R^4)_3$ ,  
wherein  $R^4$  is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl,  
30 oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

The ligand L having the general formula (C), as defined above, is a pentadentate ligand or, if  $R^1=R^2$ , can be a hexadentate ligand. As mentioned above, by 'pentadentate' is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex.

- 5 Similarly, by 'hexadentate' is meant that six hetero atoms can in principle coordinate to the metal M ion. However, in this case it is believed that one of the arms will not be bound in the complex, so that the hexadentate ligand will be penta coordinating.

- 10 In the formula (C), two hetero atoms are linked by the bridging group W and one coordinating hetero atom is contained in each of the three  $R^1$  groups. Preferably, the coordinating hetero atoms are nitrogen atoms.

- 15 The ligand L of formula (C) comprises at least one optionally substituted heteroaryl group in each of the three  $R^1$  groups. Preferably, the heteroaryl group is a pyridin-2-yl group, in particular a methyl- or ethyl-substituted pyridin-2-yl group. The heteroaryl group is linked to an N atom in formula (C), preferably *via* an alkylene group, more preferably a methylene group. Most preferably, the heteroaryl group is a 3-methyl-pyridin-2-yl group linked to an N atom *via* methylene.

- 20 The group  $R^2$  in formula (C) is a substituted or unsubstituted alkyl, aryl or arylalkyl group, or a group  $R^1$ . However, preferably  $R^2$  is different from each of the groups  $R^1$  in the formula above. Preferably,  $R^2$  is methyl, ethyl, benzyl, 2-hydroxyethyl or 2-methoxyethyl. More preferably,  $R^2$  is methyl or ethyl.

- 25 The bridging group W may be a substituted or unsubstituted alkylene group selected from  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$ ,  $-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-$ , and  $-\text{CH}_2-\text{C}_{10}\text{H}_6-\text{CH}_2-$  (wherein  $-\text{C}_6\text{H}_4-$ ,  $-\text{C}_6\text{H}_{10}-$ ,  $-\text{C}_{10}\text{H}_6-$  can be *ortho*-, *para*-, or *meta*- $\text{C}_6\text{H}_4-$ ,  $-\text{C}_6\text{H}_{10}-$ ,  $-\text{C}_{10}\text{H}_6-$ ). Preferably, the bridging group W is an ethylene or 1,4-butylene group, more preferably an ethylene group.

Preferably, V represents substituted pyridin-2-yl, especially methyl-substituted or ethyl-substituted pyridin-2-yl, and most preferably V represents 3-methyl pyridin-2-yl.

Examples of preferred ligands of formula (C) in their simplest forms are:

5

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

10 N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

15 N-(2-hydroxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-(2-methoxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-ethyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

20 N-benzyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-(2-hydroxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-(2-methoxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

25 N-ethyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-benzyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and

N-(2-methoxyethyl)-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

More preferred ligands are:

30 N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;  
 and

- 5 N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

The most preferred ligands are:

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and  
 N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

10

Preferably, the metal M in formula (A) is Fe or Mn, more preferably Fe.

- Preferred coordinating species X in formula (A) may be selected from  $R^6OH$ ,  $NR^6_3$ ,  $R^6CN$ ,  $R^6OO^-$ ,  $R^6S^-$ ,  $R^6O^-$ ,  $R^6COO^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $N_3^-$ ,  $CN^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $O^{2-}$ ,  $NO_3^-$ ,  
 15  $NO_2^-$ ,  $SO_4^{2-}$ ,  $SO_3^{2-}$ ,  $PO_4^{3-}$  and aromatic N donors selected from pyridines, pyrazines, pyrazoles, pyrroles, imidazoles, benzimidazoles, pyrimidines, triazoles and thiazoles, with  $R^6$  being selected from hydrogen, optionally substituted alkyl and optionally substituted aryl. X may also be the species  $LMO^-$  or  $LMOO^-$ , wherein M is a transition metal and L is a ligand as defined above. The coordinating species X is preferably  
 20 selected from  $CH_3CN$ ,  $H_2O$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $OOH^-$ ,  $R^6COO^-$ ,  $R^6O^-$ ,  $LMO^-$ , and  $LMOO^-$  wherein  $R^6$  represents hydrogen or optionally substituted phenyl, naphthyl, or  $C_1$ - $C_4$  alkyl.

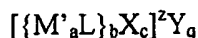
- The counter ions Y in formula (A) balance the charge z on the complex formed by the  
 25 ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as  $R^7COO^-$ ,  $BPh_4^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $R^7SO_3^-$ ,  $R^7SO_4^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ , or  $I^-$ , with  $R^7$  being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

30

Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from  $R^7COO^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $R^7SO_3^-$  (in particular  $CF_3SO_3^-$ ),  $R^7SO_4^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$ , wherein  $R^7$  represents hydrogen or optionally substituted phenyl, naphthyl or  $C_1$ - $C_4$  alkyl.

It will be appreciated that the complex (A) can be formed by any appropriate means, including *in situ* formation whereby precursors of the complex are transformed into the active complex of general formula (A) under conditions of storage or use. Preferably, the complex is formed as a well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species. Alternatively, the catalyst may be formed *in situ* from suitable precursors for the complex, for example in a solution or dispersion containing the precursor materials. In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as  $FeSO_4$  can be mixed in solution with the ligand L, or a ligand L-generating species, to form the active complex. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the substrate or wash liquor to form the active catalyst *in situ*. Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active complex according the formula (A).

Therefore, in alternative fourth and fifth embodiments, the organic substance is a compound of the general formula (D):



in which

M' represents hydrogen or a metal selected from Ti, V, Co, Zn, Mg, Ca, Sr, Ba, Na, K, and Li;

X represents a coordinating species;

a represents an integer in the range from 1 to 5;

5 b represents an integer in the range from 1 to 4;

c represents zero or an integer in the range from 0 to 5;

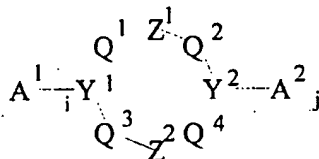
z represents the charge of the compound and is an integer which can be positive, zero or negative;

10 Y represents a counter ion, the type of which is dependent on the charge of the compound;

$q = z/[\text{charge } Y]$ ; and

L represents a pentadentate ligand of general formula (B) or (C) as defined above.

15 In a fourth embodiment of the first variant, the organic substance comprises a macrocyclic ligand of formula (E):



20 wherein

$Z^1$  and  $Z^2$  are independently selected from monocyclic or polycyclic aromatic ring structures optionally containing one or more heteroatoms, each aromatic ring structure being substituted by one or more substituents;

$Y^1$  and  $Y^2$  are independently selected from C, N, O, Si, P and S atoms;

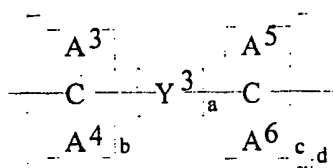
25  $A^1$  and  $A^2$  are independently selected from hydrogen, alkyl, alkenyl and cycloalkyl (each of alkyl, alkenyl and cycloalkyl) being optionally substituted by one or more groups selected from hydroxy, aryl, heteroaryl, sulphonate, phosphate, electron donating groups and electron withdrawing groups, and groups of formulae  $(G^1)(G^2)N-$ ,

$G^3OC(O)-$ ,  $G^3O-$  and  $G^3C(O)-$ , wherein each of  $G^1$ ,  $G^2$  and  $G^3$  is independently selected from hydrogen and alkyl, and electron donating and/or withdrawing groups (in addition to any amongst the foregoing);

i and j are selected from 0, 1 and 2 to complete the valency of the groups  $Y^1$  and

5  $Y^2$ ;

each of  $Q^1-Q^4$  is independently selected from groups of formula



10 wherein  $10 > a + b + c > 2$  and  $d \geq 1$ ;

each  $Y^3$  is independently selected from  $-O-$ ,  $-S-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-(G^1)N-$  (wherein  $G^1$  is hereinbefore defined),  $-C(O)-$ , arylene, heteroarylene,  $-P-$  and  $-P(O)-$ ;

each of  $A^3-A^6$  is independently selected from the groups hereinbefore defined for  $A^1$  and  $A^2$ ; and

15 wherein any two or more of  $A^1-A^6$  together form a bridging group, provided that if  $A^1$  and  $A^2$  are linked without simultaneous linking also to any of  $A^3-A^6$ , then the bridging group linking  $A^1$  and  $A^2$  must contain at least one carbonyl group.

In the ligands of formula (E), unless specifically stated to the contrary, all alkyl,

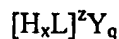
20 hydroxyalkyl alkoxy, and alkenyl groups preferably have from 1 to 6, more preferably from 1 to 4 carbon atoms.

Moreover, preferred electron donating groups include alkyl (*e.g.* methyl), alkoxy (*e.g.* methoxy), phenoxy, and unsubstituted, monosubstituted and disubstituted amine groups.

25 Preferred electron withdrawing groups include nitro, carboxy, sulphonyl and halo groups.



- The ligands of formula (E) may be used in the form of complexes with an appropriate metal or, in some cases, in non-complexed form. In the non-complexed form, they rely upon complexing with a metal supplied in the form of a separate ingredient in the composition, specifically provided for supplying that metal, or upon complexing with a metal found as a trace element in tap water. However, where the ligand alone or in complex form carries a (positive) charge, a counter anion is necessary. The ligand or complex may be formed as a neutral species but it is often advantageous, for reasons of stability or ease of synthesis, to have a charged species with appropriate anion.
- 10 Therefore, in an alternative fourth embodiment, the ligand of formula (E) is ion-paired with a counter ion, which ion-pairing is denoted by formula (F):



- 15 wherein

H is an hydrogen atom;

Y is a counter anion, the type of which is dependent on the charge of the complex;

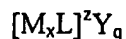
x is an integer such that one or more nitrogen atoms in L is protonated;

- 20 z represents the charge of the complex and is an integer which can be positive or zero;

$q=z/[\text{charge of } Y]$ ; and

L is a ligand of formula (E) as defined above.

- 25 In a further alternative fourth embodiment, the organic substance forms a metal complex of formula (G) based on the ion pairing of formula (F) thus:



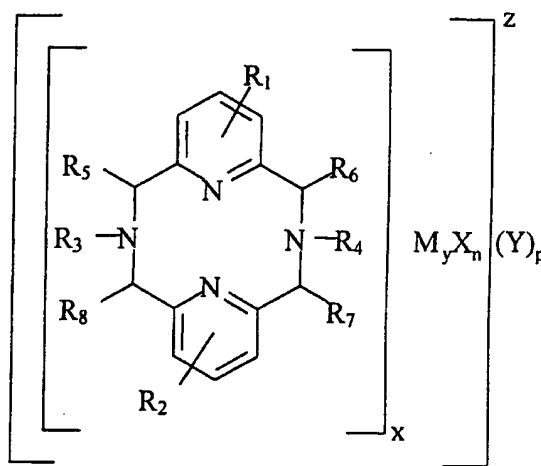
wherein L, Y, x, z and q are as defined for formula (F) above and M is a metal selected from manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III, nickel I-III, chromium II-VI, tungsten IV-VI, palladium V, ruthenium II-IV, vanadium III-IV and molybdenum IV-VI.

5

Especially preferred are the complexes of formula (G) wherein M represents manganese, cobalt, iron or copper.

In a preferred fourth embodiment, the organic substance forms a complex of the formula

10 (H):



wherein M represents an iron atom in oxidation state II or III, a manganese atom in  
 15 oxidation state II, III, IV or V, a copper atom in oxidation state I, II or III or a cobalt  
 atom in oxidation state II, III or IV, X is a group which is either a bridge or is not a  
 bridge between iron atoms, Y is a counter ion, x and y being  $\geq 1$ ,  $0 \leq n \leq 3$ , and z being  
 the charge of the metal complex, and  $p = z / \text{charge of Y}$ ;  $R_1$  and  $R_2$  being independently  
 one or more ring substituents selected from hydrogen and electron donating and  
 20 withdrawing groups,  $R_3$  to  $R_8$  being independently hydrogen, alkyl, hydroxyalkyl,  
 alkenyl or variants of any of these when substituted by one or more electron donating or  
 withdrawing groups.

For the avoidance of doubt, " $\leq$ " means "less than or equal to" and " $\geq$ " means "greater than or equal to".

- 5 Preferably, in the complex of formula (H), M represents an iron atom in oxidation state II or III or a manganese atom in oxidation state II, III, IV, or V. Preferably the oxidation state of M is III.

When M is iron, preferably the complex of formula (H) is in the form of a salt of iron  
 10 (in oxidised state) dihalo-2,11-diazo[3.3](2,6)pyridinophane, dihalo-4-methoxy-2,11-diazo[3.3] (2,6) pyridinophane and mixtures thereof, especially in the form of the chloride salt.

When M is manganese, preferably the complex of formula (H) is in the form of a salt of  
 15 manganese (in oxidised state) N, N'-dimethyl-2,11-diazo[3.3](2,6)pyridinophane, especially in the form of the monohexafluorophosphate salt.

Preferably, X is selected from  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{O}^{2-}$ ,  $\text{SH}^-$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NR}_9\text{R}_{10}^-$ ,  $\text{RCOO}^-$ ,  
 $\text{NR}_9\text{R}_{10}\text{R}_{11}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ,  $\text{N}_3^-$  and combinations thereof, wherein  $\text{R}_9$ ,  $\text{R}_{10}$  and  $\text{R}_{11}$  are  
 20 independently selected from -H,  $\text{C}_{1-4}$  alkyl and aryl optionally substituted by one or more electron withdrawing and/or donating groups. More preferably, X is a halogen, especially a fluoride ion.

In the formulae (F), (G) and (H), the anionic counter ion equivalent Y is preferably  
 25 selected from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{PF}_6^-$ ,  $\text{RSO}_3^-$ ,  $\text{RSO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BPh}_4^-$ , and  $\text{OAc}^-$ . A cationic counter ion equivalent is preferably absent.

In formula (H),  $\text{R}_1$  and  $\text{R}_2$  are preferably both hydrogen.  $\text{R}_3$  and  $\text{R}_4$  are preferably  $\text{C}_{1-4}$  alkyl, especially methyl.  $\text{R}_5$ - $\text{R}_8$  are each preferably hydrogen.

According to the values of x and y, the aforementioned preferred iron or manganese catalysts of formula (H) may be in the form of a monomer, dimer or oligomer. Without being bound by any theory, it has been conjectured that in the raw material or detergent composition state, the catalyst exists mainly or solely in monomer form but could be converted to dimer, or even oligomeric form, in the wash solution.

In typical washing compositions the level of the organic substance is such that the in-use level is from 1  $\mu$ M to 50mM, with preferred in-use levels for domestic laundry operations falling in the range 10 to 100  $\mu$ M. Higher levels may be desired and applied in industrial textile bleaching processes.

Preferably, the aqueous medium has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, still more preferably from pH 8 to 11, and most preferably from pH 8 to 10, in particular from pH 9 to 10.

The method of the present invention has particular application in detergent bleaching, especially for laundry cleaning. Accordingly, in another preferred embodiment, the method uses the organic substance in a liquor that additionally contains a surface-active material, optionally together with detergency builder.

The bleach liquor may for example contain a surface-active material in an amount of from 10 to 50% by weight. The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher aryl

- groups. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl (C<sub>10</sub>-C<sub>15</sub>)
- 5 benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C<sub>9</sub>-C<sub>18</sub>) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction
- 10 products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived by reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolysing with a base to produce a random
- 15 sulphonate; sodium and ammonium (C<sub>7</sub>-C<sub>12</sub>) dialkyl sulphosuccinates; and olefin sulphonates, which term is used to describe material made by reacting olefins, particularly (C<sub>10</sub>-C<sub>20</sub>) alpha-olefins, with SO<sub>3</sub> and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C<sub>10</sub>-C<sub>15</sub>) alkylbenzene sulphonates, and sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl ether sulphates.
- 20 Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C<sub>6</sub>-C<sub>22</sub>) phenols, generally 5-25 EO, *i.e.* 5-25 units of ethylene oxides per molecule; and the condensation
- 25 products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the

30 compositions of the invention but this is not normally desired owing to their relatively

high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

- 5 The detergent bleach liquor will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant. In a further preferred embodiment, the detergent active system is free from C<sub>16</sub>-C<sub>12</sub> fatty acid soaps.

- 10 The bleach liquor may also contains a detergency builder, for example in an amount of from about 5 to 80 % by weight, preferably from about 10 to 60 % by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

- 15 Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

20

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

- 25 Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, *e.g.* zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

- 30 In particular, the bleach liquor may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted

or only used in very small amounts. Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can  
5 be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferably not more than 2.5 % by weight  
10 to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Apart from the components already mentioned, the bleach liquor can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers  
15 such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (*i.e.* Dequest® types); fabric softening agents; inorganic  
20 salts and alkaline buffering agents, such as sodium sulphate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

Transition metal sequestrants such as EDTA, and phosphonic acid derivatives such as  
25 EDTMP (ethylene diamine tetra(methylene phosphonate)) may also be included, in addition to the organic substance specified, for example to improve the stability sensitive ingredients such as enzymes, fluorescent agents and perfumes, but provided the composition remains bleaching effective. However, the treatment composition containing the organic substance, is preferably substantially, and more preferably  
30 completely, devoid of transition metal sequestrants (other than the organic substance).

Whilst the present invention is based on the catalytic bleaching of a substrate by atmospheric oxygen or air, it will be appreciated that small amounts of hydrogen peroxide or peroxy-based or -generating systems may be included in the treatment composition, if desired. Preferably, however, the composition will be devoid of peroxygen bleach or peroxy-based or -generating bleach systems.

The invention will now be further illustrated by way of the following non-limiting examples:

10



## EXAMPLES

### Example 1

- 5 This example describes a synthesis of a catalyst according to formula (A):

#### **(i) Preparation of MeN4Py ligand:**

The precursor N4Py.HClO<sub>4</sub> was prepared as follows:

- 10 To pyridyl ketone oxim (3 g, 15.1 mmol) was added ethanol (15 ml), concentrated ammonia solution (15 mL) and NH<sub>4</sub>OAc (1.21 g, 15.8 mmol). The solution was warmed until reflux. To this solution was added 4.64 g Zn in small portions. After the addition of all Zn, the mixture was refluxed for 1 hour and allowed to cool to ambient temperature. The solution was filtered and water (15 ml) was added. Solid NaOH was
- 15 added until pH>>10 and the solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 ml). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated until dryness. Bis(pyridin-2-yl)methylamine (2.39 g, 12.9 mmol) was obtained as a colourless oil in 86% yield, showing the following analytical characteristics:
- 20 <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>): δ 2.64 (s, 2H, NH<sub>2</sub>), 5.18 (s, 1H, CH), 6.93 (m, 2H, pyridine), 7.22 (m, 2H, pyridine), 7.41 (m, 2H, pyridine), 8.32 (m, 2H, pyridine); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 62.19 (CH), 121.73 (CH), 122.01 (CH), 136.56 (CH), 149.03 (CH), 162.64 (Cq).

- To picolylchloride hydrochloride (4.06 g, 24.8 mmol) was added, at 0°C, 4.9 ml of a 5N
- 25 NaOH solution. This emulsion was added by means of a syringe to bis(pyridin-2-yl)methylamine (2.3 g, 12.4 mmol) at 0°C. Another 5 ml of a 5N NaOH solution was added to this mixture. After warming to ambient temperature, the mixture was stirred vigorously for 40 hrs. The mixture was put in an ice bath and HClO<sub>4</sub> was added until pH<1, whereupon a brown solid precipitated. The brown precipitate was collected by
- 30 filtration and recrystallized from water. While stirring, this mixture was allowed to cool

to ambient temperature, whereupon a light-brown solid precipitated which was collected by filtration and washed with cold water and air-dried (1.47 g).

From 0.5 g of the perchlorate salt of N4Py prepared as described above, the free amine  
5 was obtained by precipitating the salt with 2N NaOH and subsequently by extraction with CH<sub>2</sub>Cl<sub>2</sub>. To the free amine was added under argon 20 ml of dry tetrahydrofuran freshly distilled from LiAlH<sub>4</sub>. The mixture was stirred and cooled to -70 °C by an alcohol / dry ice bath. Now 1 ml of 2.5 N butyllithium solution in hexane was added giving an immediate dark red colour. The mixture was allowed to warm to -20 °C and  
10 now 0.1 ml of methyl iodide was added. The temperature was kept to -10 °C for 1 hour. Subsequently 0.5 g of ammonium chloride was added and the mixture was evaporated in vacuo. To the residue water was added and the aqueous layer was extracted with dichloromethane. The dichloromethane layer was dried on sodium sulphate, filtered and evaporated giving 0.4 g residue. The residue was purified by crystallisation from ethyl  
15 acetate and hexane giving 0.2 g of creamish powder (50% yield) showing the following analytical characteristics:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 2.05 (s, 3H, CH<sub>3</sub>), 4.01 (s, 4H, CH<sub>2</sub>), 6.92 (m, 2H, pyridine), 7.08 (m, 2H, pyridine), 7.39 (m, 4H pyridine), 7.60 (m 2H, pyridine), 7.98 (d, 2H, pyridine), 8.41 (m, 2H pyridine), 8.57 (m, 2H, pyridine). <sup>13</sup>C NMR (100.55  
20 MHz, CDCl<sub>3</sub>): δ (ppm) 21.7 (CH<sub>3</sub>), 58.2 (CH<sub>2</sub>), 73.2 (Cq), 121.4 (CH), 121.7 (CH), 123.4 (CH), 123.6 (CH), 136.0 (CH), 148.2 (Cq), 148.6 (Cq), 160.1 (Cq), 163.8 (Cq).

**(ii) Synthesis of the complex [(MeN4Py)Fe(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> , Fe(MeN4Py):**

25 To a solution of 0.27 g of MeN4Py in 12 ml of a mixture of 6 ml acetonitrile and 6 ml methanol was added 350 mg Fe(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O immediately a dark red colour formed. To the mix was added now 0.5 g of sodium perchlorate and a orange red precipitate formed immediately. After 5 minutes stirring and ultrasonic treatment the precipitate was isolated by filtration and dried in vacuo at 50°C. In this way 350 mg of an orange red  
30 powder was obtained in 70% yield showing the following analytical characteristics:

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) 2.15, ( $\text{CH}_3\text{CN}$ ), 2.28 (s, 3H,  $\text{CH}_3$ ), 4.2 (ab, 4H,  $\text{CH}_2$ ), 7.05 (d, 2H, pyridine), 7.38 (m, 4H, pyridine), 7.71 (2t, 4H pyridine), 7.98 (t, 2H, pyridine), 8.96 (d, 2H pyridine), 9.06 (m, 2H, pyridine).

UV/Vis (acetonitrile) [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ )]: 381 (8400), 458 nm (6400).

5    Anal. Calcd for  $\text{C}_{25}\text{H}_{26}\text{Cl}_2\text{FeN}_6\text{O}_8$ : C, 46.11; H, 3.87; N, 12.41; Cl, 10.47; Fe, 8.25.

Found: C, 45.49; H, 3.95; N, 12.5; Cl, 10.7; Fe, 8.12.

Mass-ESP (cone voltage 17V in  $\text{CH}_3\text{CN}$ ):  $m/z$  218.6 [ $\text{MeN4PyFe}$ ] $^{2+}$ ; 239.1 [ $\text{MeN4PyFeCH}_3\text{CN}$ ] $^{2+}$ .

## 10    **Example 2**

This example describes a synthesis of a catalyst according to formula (A):

### (i) Synthesis of BzN4Py ligand:

15

To 1 g of the N4Py ligand prepared as described above, 20 ml of dry tetrahydrofuran freshly distilled from  $\text{LiAlH}_4$ , was added under argon. The mixture was stirred and cooled to  $-70^\circ\text{C}$  by an alcohol / dry ice bath. Now 2 ml of 2.5 N butyllithium solution in hexane was added giving an immediate dark red colour. The mix was allowed to warm  
20 to  $-20^\circ\text{C}$  and now 0.4 ml of benzyl bromide was added. The mixture was allowed to warm up to  $25^\circ\text{C}$  and stirring was continued over night. Subsequently 0.5 g of ammonium chloride was added and the mixture was evaporated in vacuo. To the residue water was added and the aqueous layer was extracted with dichloromethane. The dichloromethane layer was dried on sodium sulphate, filtered and evaporated giving 1 g  
25 brown oily residue. According to NMR spectroscopy, the product was not pure but contained no starting material (N4Py). The residue was used without further purification.

### (ii) Synthesis of the complex $[(\text{BzN4Py})\text{Fe}(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ , $\text{Fe}(\text{BzN4Py})$ :

30

To a solution of 0.2 g of the residue obtained by the previous described procedure in 10 ml of a mixture of 5 ml acetonitrile and 5 ml methanol was added 100 mg  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  immediately a dark red colour formed. To the mix was added now 0.25 g of sodium perchlorate and ethylacetate was allowed to diffuse into the mixture  
5 overnight. Some red crystals were formed which were isolated by filtration and washed with methanol. In this way 70 mg of a red powder was obtained showing the following analytical characteristics:

$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) 2.12, (s, 3H,  $\text{CH}_3\text{CN}$ ), 3.65 + 4.1 (ab, 4H,  $\text{CH}_2$ ), 4.42 (s, 2H,  $\text{CH}_2$ -benzyl), 6.84 (d, 2H, pyridine), 7.35 (m, 4H, pyridine), 7.45 (m, 3 H, benzene) 7.65 (m, 4H benzene + pyridine), 8.08(m, 4H, pyridine), 8.95 (m, 4H pyridine).  
10

UV/Vis (acetonitrile) [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 380 (7400), 458 nm (5500).

Mass-ESP (cone voltage 17V in  $\text{CH}_3\text{CN}$ ):  $m/z$  256.4 [ $\text{BzN}_4\text{Py}$ ] $^{2+}$ ; 612

[ $\text{BzN}_4\text{PyFeClO}_4$ ] $^{+}$   
15

### **Example 3:**

This example describes syntheses of catalysts according to formula (C):

20 All reactions were performed under a nitrogen atmosphere, unless indicated otherwise. All reagents and solvents were obtained from Aldrich or Across and used as received, unless stated otherwise. Petroleum ether 40-60 was distilled using a rotavapor before using it as eluent. Flash column chromatography was performed using Merck silica gel 60 or aluminium oxide 90 (activity II-III according to Brockmann).  $^1\text{H}$  NMR (300  
25 MHz) and  $^{13}\text{C}$  NMR (75 MHz) were recorded in  $\text{CDCl}_3$ , unless stated otherwise. Multiplicities were addressed with the normal abbreviations using p for quintet.

### **Synthesis of starting materials for ligand synthesis:**

30 **Synthesis of *N*-benzyl amino acetonitrile.** *N*-benzyl amine (5.35 g, 50 mmol) was dissolved in a water : methanol mixture (50 mL, 1:4). Hydrochloric acid (aq., 30 %)

was added until the pH reached 7.0. Added was NaCN (2.45 g, 50 mmol). After cooling to 0 °C, formaline (aq. 35 %, 4.00 g, 50 mmol) was added. The reaction was followed by TLC (aluminium oxide; EtOAc : Et<sub>3</sub>N = 9:1) until benzylamine could be detected. Subsequently the methanol was evaporated *in vacuo* and the remaining oil  
5 "dissolved" in water. The aqueous phase was extracted with methylene chloride (3 x 50 mL). The organic layers were collected and the solvent removed *in vacuo*. The residue was purified by Kugelrohr distillation (p = 20 mm Hg, T = 120 °C) giving *N*-benzyl amino acetonitrile (4.39 g, 30 mmol, 60 %) as a colourless oil.

<sup>1</sup>H NMR: δ 7.37 - 7.30 (m, 5H), 3.94 (s, 2H), 3.57 (s, 2H), 1.67 (br s, 1H);  
10 <sup>13</sup>C NMR: δ 137.74, 128.58, 128.46, 128.37, 127.98, 127.62, 117.60, 52.24, 36.19.

**Synthesis of *N*-ethyl amino acetonitrile.** This synthesis was performed analogously to the synthesis reported for *N*-benzyl amino acetonitrile. However, detection was done by dipping the TLC plate in a solution of KMnO<sub>4</sub> and heating the plate until bright spots  
15 appeared. Starting from ethylamine (2.25 g, 50 mmol), pure *N*-ethyl amino acetonitrile (0.68 g, 8.1 mmol, 16 %) was obtained as a slightly yellow oil.

<sup>1</sup>H NMR: δ 3.60 (s, 2H), 2.78 (q, *J* = 7.1, 2H), 1.22 (br s, 1H), 1.14 (t, *J* = 7.2, 3H);  
<sup>13</sup>C NMR: δ 117.78, 43.08, 37.01, 14.53.

20 **Synthesis of *N*-ethyl ethylene-1,2-diamine.** The synthesis was performed according to Hageman; J.Org.Chem.; 14; 1949; 616, 634, starting from *N*-ethyl amino acetonitrile.

**Synthesis of *N*-benzyl ethylene-1,2-diamine.** Sodium hydroxide (890 mg; 22.4 mmol) was dissolved in ethanol (96 %, 20 mL), the process taking the better part of 2 hours.  
25 Added was *N*-benzyl amino acetonitrile (4, 2.92 g, 20 mmol) and Raney Nickel (approx. 0.5 g). Hydrogen pressure was applied (p = 3.0 atm.) until hydrogen uptake ceased. The mixture was filtered over Cellite, washing the residue with ethanol. The filter should not run dry since Raney Nickel is relatively pyrophoric. The Cellite containing the Raney Nickel was destroyed by putting the mixture in dilute acid, causing gas  
30 formation). The ethanol was evaporated in *in vacuo* and the residue dissolved in water.

Upon addition of base (aq. NaOH, 5N) the product oiled out and was extracted with chloroform (3 x 20 mL). After evaporation of the solvent *in vacuo* the <sup>1</sup>H NMR showed the presence of benzylamine. Separation was enforced by column chromatography (silica gel; MeOH : EtOAc : Et<sub>3</sub>N = 1:8:1) yielding the benzyl amine, followed by the solvent mixture MeOH : EtOAc : Et<sub>3</sub>N = 5:4:1. Detection was done by using aluminium oxide as a solid phase in TLC, yielding pure *N*-benzyl ethylene-1,2-diamine (2.04 g, 13.6 mmol, 69 %).

<sup>1</sup>H NMR: δ 7.33 - 7.24 (m, 5H), 3.80 (s, 2H), 2.82 (t, *J* = 5.7, 2H), 2.69 (t, *J* = 5.7, 2H), 1.46 (br s, 3H);

<sup>13</sup>C NMR: δ 140.37, 128.22, 127.93, 126.73, 53.73, 51.88, 41.66.

**Synthesis of 2-acetoxymethyl-5-methyl pyridine.** 2,5-Lutidine (31.0 g, 290 mmol), acetic acid (180 mL) and hydrogen peroxide (30 mL, 30 %) were heated at 70-80 °C for 3 hours. Hydrogen peroxide (24 mL, 30 %) was added and the subsequent mixture heated for 16 hours at 60-70 °C. Most of the mixture of (probably) hydrogen peroxide, water, acetic acid, and peracetic acid was removed *in vacuo* (rotavap, water bath 50 °C until *p* = 20 mbar). The resulting mixture containing the *N*-oxide was added dropwise to acetic anhydride heated under reflux. This reaction was highly exothermic, and was controlled by the dropping speed. After heating under reflux for an hour, methanol was added dropwise. This reaction was highly exothermic. The resulting mixture was heated under reflux for another 30 minutes. After evaporation of the methanol (rotavap, 50 °C until *p* = 20 mbar), the resulting mixture was purified by Kugelrohr distillation (*p* = 20 mm Hg, *T* = 150 °C). The clear oil that was obtained still contained acetic acid. This was removed by extraction (CH<sub>2</sub>Cl<sub>2</sub>, NaHCO<sub>3</sub> (sat.)) yielding the pure acetate of 2-acetoxymethyl-5-methyl pyridine (34.35 g, 208 mmol, 72 %) as a slightly yellow oil.

<sup>1</sup>H NMR: δ 8.43 (s, 1H), 7.52 (dd, *J* = 7.8, *J* = 1.7, 1H), 7.26 (d, *J* = 7.2, 1H), 5.18 (s, 2H), 2.34 (s, 3H), 2.15 (s, 3H);

<sup>13</sup>C NMR: δ 170.09, 152.32, 149.39, 136.74, 131.98, 121.14, 66.31, 20.39, 17.66.

**Synthesis of 2-acetoxymethyl-5-ethyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-acetoxymethyl-5-methyl pyridine. Starting from 5-ethyl-2-methyl pyridine (35.10 g, 290 mmol), pure 2-acetoxymethyl-5-ethyl pyridine (46.19 g, 258 mmol, 89%) was obtained as a slightly yellow oil.

5  $^1\text{H}$  NMR:  $\delta$  8.47 (s, 1H), 7.55 (d,  $J = 7.8$ , 1H), 7.29 (d,  $J = 8.1$ , 1H), 2.67 (q,  $J = 7.8$ , 2H), 2.14 (s, 3H), 1.26 (t,  $J = 7.77$ , 3H);

$^{13}\text{C}$  NMR:  $\delta$  170.56, 152.80, 149.11, 138.47, 135.89, 121.67, 66.72, 25.65, 20.78, 15.13.

10 **Synthesis of 2-acetoxymethyl-3-methyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-acetoxymethyl-5-methyl pyridine. The only difference was the reversal of the Kugelrohr distillation and the extraction. According to  $^1\text{H}$  NMR a mixture of the acetate and the corresponding alcohol was obtained. Starting from 2,3-picoline (31.0 g, 290 mmol), pure 2-acetoxymethyl-3-methyl pyridine  
15 (46.19 g, 258 mmol, 89%, calculated for pure acetate) was obtained as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.45 (d,  $J = 3.9$ , 1H), 7.50 (d,  $J = 8.4$ , 1H), 7.17 (dd,  $J = 7.8$ ,  $J = 4.8$ , 1H), 5.24 (s, 2H), 2.37 (s, 3H), 2.14 (s, 3H).

20 **Synthesis of 2-hydroxymethyl-5-methyl pyridine.** 2-Acetoxymethyl-5-methyl pyridine (30 g, 182 mmol) was dissolved in hydrochloric acid (100 mL, 4 N). The mixture was heated under reflux, until TLC (silica gel; triethylamine:ethyl acetate:petroleum ether 40-60 = 1:9:19) showed complete absence of the acetate (normally 1 hour). The mixture was cooled, brought to pH > 11, extracted with  
25 dichloromethane (3 x 50 mL) and the solvent removed *in vacuo*. Pure 2-hydroxymethyl-5-methyl pyridine (18.80 g, 152 mmol, 84 %) was obtained by Kugelrohr distillation ( $p = 20$  mm Hg,  $T = 130$  °C) as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.39 (s, 1H), 7.50 (dd,  $J = 7.8$ ,  $J = 1.8$ , 1H), 7.15 (d,  $J = 8.1$ , 1H), 4.73 (s, 2H), 3.83 (br s, 1H), 2.34 (s, 3H);

30  $^{13}\text{C}$  NMR:  $\delta$  156.67, 148.66, 137.32, 131.62, 120.24, 64.12, 17.98.

**Synthesis of 2-hydroxymethyl-5-ethyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-hydroxymethyl-5-methyl pyridine. Starting from 2-acetoxymethyl-5-ethyl pyridine (40 g, 223 mmol), pure 2-hydroxymethyl-5-ethyl pyridine (26.02 g, 189 mmol, 85 %) was obtained as a slightly yellow oil.

<sup>1</sup>H NMR: δ 8.40 (d, *J* = 1.2, 1H), 7.52 (dd, *J* = 8.0, *J* = 2.0, 1H), 7.18 (d, *J* = 8.1, 1H), 4.74 (s, 2H), 3.93 (br s, 1H), 2.66 (q, *J* = 7.6, 2H), 1.26 (t, *J* = 7.5, 3H);

<sup>13</sup>C NMR: δ 156.67, 148.00, 137.87, 136.13, 120.27, 64.07, 25.67, 15.28.

**Synthesis of 2-hydroxymethyl-3-methyl pyridine.** This synthesis was performed analogously to the synthesis reported for 2-hydroxymethyl-5-methyl pyridine. Starting from 2-acetoxymethyl-3-methyl pyridine (25g (recalculated for the mixture), 152 mmol), pure 2-hydroxymethyl-3-methyl pyridine (15.51 g, 126 mmol, 83 %) was obtained as a slightly yellow oil.

<sup>1</sup>H NMR: δ 8.40 (d, *J* = 4.5, 1H), 7.47 (d, *J* = 7.2, 1H), 7.15 (dd, *J* = 7.5, *J* = 5.1, 1H), 4.85 (br s, 1H), 4.69 (s, 1H), 2.22 (s, 3H);

<sup>13</sup>C NMR: δ 156.06, 144.97, 137.38, 129.53, 121.91, 61.38, 16.30.

(i) Synthesis of ligands:

20

**Synthesis of *N*-methyl-*N,N,N*-tris(pyridin-2-ylmethyl)ethylene-1,2-diamine (L1).**

The ligand L1 (comparative) was prepared according to Bernal, Ivan; Jensen, Inge Margrethe; Jensen, Kenneth B.; McKenzie, Christine J.; Toftlund, Hans; Tuchagues, Jean-Pierre; J.Chem.Soc.Dalton Trans.; 22; 1995; 3667-3676.

25

**Synthesis of *N*-methyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L2, MeTrilen).** 2-Hydroxymethyl-3-methyl pyridine (5.00 g, 40.7 mmol) was dissolved in dichloromethane (30 mL). Thionyl chloride (30 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 hour and the solvents removed *in vacuo* (rotavap, until *p* = 20 mm Hg, *T* = 50 °C). To the resultant mixture

30



- was added dichloromethane (25 mL). Subsequently NaOH (5 N, aq.) was added dropwise until the pH (aqua)  $\geq 11$ . The reaction was quite vigorous in the beginning, since part of the thionyl chloride was still present. *N*-methyl ethylene-1,2-diamine (502 mg, 6.8 mmol) and additional NaOH (5 N, 10 mL) were added. The reaction
- 5 mixture was stirred at room temperature for 45 hours. The mixture was poured into water (200 mL), and the pH checked ( $\geq 14$ , otherwise addition of NaOH (aq. 5N)). The reaction mixture was extracted with dichloromethane (3 or 4 x 50 mL, until no product could be detected by TLC). The combined organic phases were dried and the solvent removed *in vacuo*. Purification was enforced as described before, yielding *N*-methyl-
- 10 *N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine as a slightly yellow oil. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate : petroleum ether 40-60 = 1:9:10) until the impurities were removed according to TLC (aluminium oxide, same eluent,  $R_f \approx 0.9$ ). The compound was eluted using ethylacetate : triethyl amine = 9:1.
- 15 *N*-methyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L2, 1.743 g, 4.30 mmol, 63 %) was obtained.
- $^1\text{H}$  NMR:  $\delta$  8.36 (d,  $J = 3.0$ , 3H), 7.40 - 7.37 (m, 3H), 7.11-7.06 (m, 3H), 3.76 (s, 4H), 3.48 (s, 2H), 2.76 - 2.71 (m, 2H), 2.53 - 2.48 (m, 2H), 2.30 (s, 3H), 2.12 (s, 6H), 2.05 (s, 3H);
- 20  $^{13}\text{C}$  NMR:  $\delta$  156.82, 156.77, 145.83, 145.67, 137.61, 133.14, 132.72, 122.10, 121.88, 62.32, 59.73, 55.19, 51.87, 42.37, 18.22, 17.80.

**Synthesis of *N*-ethyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L3, EtTrilen).** This synthesis is performed analogously to the synthesis for L2.

- 25 Starting from 2-hydroxymethyl-3-methyl pyridine (25.00 g, 203 mmol) and *N*-ethyl ethylene-1,2-diamine (2.99 g, 34.0 mmol), *N*-ethyl-*N,N,N*-tris(methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L3, 11.49 g, 28.5 mmol, 84 %) was obtained. Column chromatography (aluminium oxide; Et<sub>3</sub>N : EtOAc : petroleum ether 40-60 = 1:9:30, followed by Et<sub>3</sub>N : EtOAc = 1:9).

<sup>1</sup>H NMR: δ 8.34 - 8.30 (m, 3H), 7.40 - 7.34 (m, 3H), 7.09 - 7.03 (m, 3H), 3.71 (s, 4H), 3.58 (s, 2H), 2.64 - 2.59 (m, 2H), 2.52 - 2.47 (m, 2H), 2.43 - 2.36 (m, 2H), 2.31 (s, 3H), 2.10 (s, 6H), 0.87 (t, *J* = 7.2, 3H);

<sup>13</sup>C NMR: δ 157.35, 156.92, 145.65, 137.61, 133.14, 132.97, 122.09, 121.85, 59.81, 59.28, 51.98, 50.75, 48.02, 18.27, 17.80, 11.36.

**Synthesis of *N*-benzyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L4, BzTrilen).** This synthesis is performed analogously to the synthesis for L2. Starting from 2-hydroxymethyl-3-methylpyridine (3.00 g 24.4 mmol), and *N*-benzyl ethylene-1,2-diamine (610 mg, 4.07 mmol), *N*-benzyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L4, 1.363 g, 2.93 mmol, 72 %) was obtained. Column chromatography (aluminium oxide; Et<sub>3</sub>N : EtOAc : petroleum ether 40-60 = 1:9:10).

<sup>1</sup>H NMR: δ 8.33 - 8.29 (m, 3H), 7.37 - 7.33 (m, 3H), 7.21 - 7.03 (m, 8H), 3.66 (s, 4H), 3.60 (s, 2H), 3.42 (s, 2H), 2.72 - 2.67 (m, 2H), 2.50 - 2.45 (m, 2H), 2.23 (s, 3H), 2.03 (s, 6H);

<sup>13</sup>C NMR: δ 157.17, 156.96, 145.83, 145.78, 139.29, 137.91, 137.80, 133.45, 133.30, 128.98, 127.85, 126.62, 122.28, 122.22, 59.99, 58.83, 51.92, 51.54, 18.40, 17.95.

**Synthesis of *N*-hydroxyethyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L5).** This synthesis is performed analogously to the synthesis for L6. Starting from 2-hydroxymethyl-3-methyl pyridine (3.49 g, 28.4 mmol), and *N*-hydroxyethyl ethylene-1,2-diamine (656 mg 6.30 mmol), after 7 days *N*-hydroxyethyl-*N,N',N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L5, 379 mg, 0.97 mmol, 14 %) was obtained.

<sup>1</sup>H NMR: δ 8.31 - 8.28 (m, 3H), 7.35 - 7.33 (m, 3H), 7.06 - 7.00 (m, 3H), 4.71 (br s, 1H), 3.73 (s, 4H), 3.61 (s, 2H), 3.44 (t, *J* = 5.1, 2H), 2.68 (s, 4H), 2.57 (t, *J* = 5.0, 2H), 2.19 (s, 3H), 2.10 (s, 6H);

<sup>13</sup>C NMR: δ 157.01, 156.88, 145.91, 145.80, 137.90, 137.83, 133.30, 131.89, 122.30, 121.97, 59.60, 59.39, 57.95, 56.67, 51.95, 51.22, 18.14, 17.95.

**Synthesis of *N*-methyl-*N,N,N*-tris(5-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L6).** 2-hydroxymethyl-5-methyl pyridine (2.70 g, 21.9 mmol) was dissolved in dichloromethane (25 mL). Thionyl chloride (25 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 hour and the solvents removed *in vacuo* (rotavap, until  $p = 20$  mm Hg,  $T \pm 35^\circ\text{C}$ ). The remaining oil was used directly in the synthesis of the ligands, since it was known from the literature that the free picolyl chlorides are somewhat unstable and are highly lachrymatory. To the resultant mixture was added dichloromethane (25 mL) and *N*-methyl ethylene-1,2-diamine (360 mg, 4.86 mmol). Subsequently NaOH (5 N, aq.) was added dropwise. The reaction was quite vigorous in the beginning, since part of the thionyl chloride was still present. The aqueous layer was brought to pH = 10, and additional NaOH (5 N, 4.38 mL) was added. The reaction mixture was stirred until a sample indicated complete conversion (7 days). The reaction mixture was extracted with dichloromethane (3 x 25 mL). The combined organic phases were dried and the solvent removed *in vacuo*. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate : petroleum ether 40-60 = 1:9:10) until the impurities were removed according to TLC (aluminium oxide, same eluent,  $R_f \approx 0.9$ ). The compound was eluted using ethyl acetate : triethyl amine = 9:1, yielding *N*-methyl-*N,N,N*-tris(5-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L6, 685 mg, 1.76 mmol, 36 %) as a slightly yellow oil.

$^1\text{H}$  NMR:  $\delta$  8.31 (s, 3H) 7.43 - 7.35 (m, 5H), 7.21 (d,  $J = 7.8$ , 1H), 3.76 (s, 4H), 3.56 (s, 2H), 2.74 - 2.69 (m, 2H), 2.63 - 2.58 (m, 2H), 2.27 (s, 6H), 2.16 (s, 3H);

$^{13}\text{C}$  NMR:  $\delta$  156.83, 156.43, 149.23, 149.18, 136.85, 136.81, 131.02, 122.41, 122.30, 63.83, 60.38, 55.53, 52.00, 42.76, 18.03.

**Synthesis of *N*-methyl-*N,N,N*-tris(5-ethylpyridin-2-ylmethyl)ethylene-1,2-diamine (L7).** This synthesis is performed analogously to the synthesis for L6. Starting from 2-hydroxymethyl-5-ethyl pyridine (3.00 g, 21.9 mmol), and *N*-methyl ethylene-1,2-

diamine (360 mg, 4.86 mmol), after 7 days *N*-methyl-*N,N,N*-tris(5-ethylpyridin-2-ylmethyl)ethylene-1,2-diamine (**L7**, 545 mg, 1.26 mmol, 26 %) was obtained.

<sup>1</sup>H NMR: δ 8.34 (s, 3H), 7.44 - 7.39 (m, 5H), 7.26 (d, *J* = 6.6, 1H), 3.80 (s, 4H), 3.59 (s, 2H), 2.77 - 2.72 (m, 2H), 2.66 - 2.57 (m, 8H), 2.18 (s, 3H), 1.23 (t, *J* = 7.5, 9H);

5 <sup>13</sup>C NMR: δ 157.14, 156.70, 148.60, 148.53, 137.25, 135.70, 122.59, 122.43, 63.91, 60.48, 55.65, 52.11, 42.82, 25.73, 15.36.

(ii) Synthesis of metal-ligand complexes:

10

**Synthesis of *N*-methyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF<sub>6</sub> ([**L2** Fe(II)Cl]PF<sub>6</sub>).** FeCl<sub>2</sub>.4H<sub>2</sub>O (51.2 mg, 257 μmol) was dissolved in MeOH : H<sub>2</sub>O = 1:1 (2.5 mL). The solution was heated to 50 °C.

Added was *N*-methyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine  
15 (**L2**, 100 mg, 257 μmol) in MeOH : H<sub>2</sub>O = 1:1 (2.0 mL). Subsequently NaPF<sub>6</sub> (86.4 mg, 514 μmol) in H<sub>2</sub>O (2.5 mL) was added dropwise. Cooling to room temperature, filtration and drying *in vacuo* (p = 0.05 mm Hg, T = room temperature) yielded the complex [**L2** Fe(II)Cl]PF<sub>6</sub> (149 mg, 239 μmol, 93 %) as a yellow solid.

<sup>1</sup>H NMR (CD<sub>3</sub>CN, paramagnetic): δ 167.17, 142.18, 117.01, 113.34, 104.79, 98.62,  
20 70.77, 67.04, 66.63, 58.86, 57.56, 54.49, 51.68, 48.56, 45.90, 27.99, 27.36, 22.89, 20.57, 14.79, 12.14, 8.41, 8.16, 7.18, 6.32, 5.78, 5.07, 4.29, 3.82, 3.43, 2.91, 2.05, 1.75, 1.58, 0.94, 0.53, -0.28, -1.25, -4.82, -18.97, -23.46.

**Synthesis of *N*-ethyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF<sub>6</sub> ([**L3** Fe(II)Cl]PF<sub>6</sub>).** This synthesis was performed analogously to the synthesis for [**L2** Fe(II)Cl]PF<sub>6</sub>. Starting from *N*-ethyl-*N,N,N*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (**L3**, 104 mg, 257 μmol) gave the complex [**L3** Fe(II)Cl]PF<sub>6</sub> (146 mg, 229 μmol, 89%) as a yellow solid.

25

$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , paramagnetic):  $\delta$  165.61, 147.20, 119.23, 112.67, 92.92, 63.14, 57.44, 53.20, 50.43, 47.80, 28.59, 27.09, 22.48, 8.55, 7.40, 3.63, 2.95, 2.75, 2.56, 2.26, 1.75, 1.58, 0.92, 0.74, -0.28, -1.68, -2.68, -12.36, -28.75.

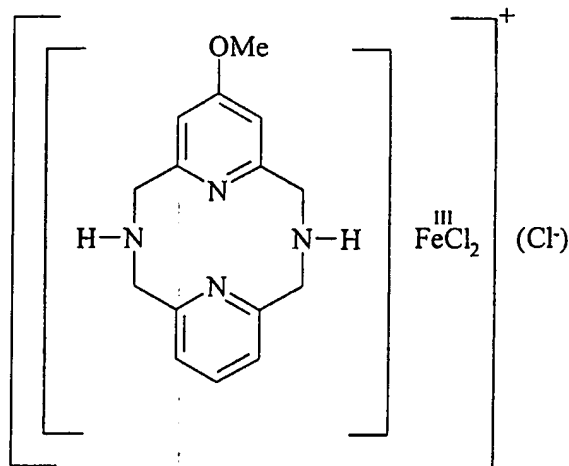
- 5 **Synthesis of *N*-benzyl-*N,N,N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF<sub>6</sub> ([L4 Fe(II)Cl]PF<sub>6</sub>).** This synthesis was performed analogously to the synthesis for [L2 Fe(II)Cl]PF<sub>6</sub>. Starting from *N*-benzyl-*N,N,N'*-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (L4, 119.5 mg, 257  $\mu\text{mol}$ ) gave the complex (172 mg, 229  $\mu\text{mol}$ , 95 %) as a yellow solid.

- 10  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , paramagnetic):  $\delta$  166.33, 145.09, 119.80, 109.45, 92.94, 57.59, 52.83, 47.31, 28.40, 27.89, 16.28, 11.05, 8.70, 8.45, 7.69, 6.99, 6.01, 4.12, 2.89, 2.71, 1.93, 1.56, -0.28, -1.68, -2.58, -11.40, -25.32.

#### Example 4

15

This example describes a synthesis of a catalyst of formula (H) wherein:-



- 20  $\text{R}_2\text{-R}_8=\text{H}$ ;  $\text{R}_1=4\text{-MeO}$ ;  $x=1$ ;  $y=1$ ;  $z=1$ ;  $\text{X}=\text{Cl}$ ,  $n=2$ ;  $\text{Y}=\text{Cl}^-$ ,  $p=1$ .

(i) Synthesis of the ligand 2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane  
((4OMe)LN<sub>4</sub>H<sub>2</sub>):

- 5 4-chloro-2,6-pyridyl dimethyl ester (2). A mixture of 4-hydroxy-2,6-pyridine dicarboxylic acid (12.2 g, 60 mmoles) and PCl<sub>5</sub> (41.8g, 200 mmoles) in 100 ml of CCl<sub>4</sub> was refluxed until the evolution of HCl ceased. Absolute methanol (50ml) was slowly added. After cooling, all the volatile material was removed. The mixture was then poured into 200 ml of water and ice. The diester crystallised immediately and was collected by filtration (70%). <sup>1</sup>H NMR (200MHz, H<sub>2</sub>O) δ 7.60 (2H,s), 4.05 (6H, s).
- 10 4-methoxy-2,6-pyridine dimethanol (4). Metallic sodium (1g, 44 mmoles) was dissolved into 200 ml of dry methanol. 4-chloro-2,6-pyridyl dimethyl ester (9.2 g, 40 mmoles) was then added and the mixture was refluxed for 3 hours to obtain pure 4-methoxy-2,6-pyridyl dimethyl ester. To this solution, at RT, NaBH<sub>4</sub> (9.1 g, 240 mmoles) was added
- 15 in small portions and the mixture was refluxed for 16 hours. Acetone (30 ml) was then added and the solution refluxed for an additional 1 hour. After all the volatile material was removed, the residue was heated with 60 ml of a saturated NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> solution. After dilution with 80 ml of water, the product was continuously extracted with CHCl<sub>3</sub> for 2-3 days. Evaporation of the CHCl<sub>3</sub> yielded 83 % of 4-methoxy-2,6-
- 20 pyridine dimethanol. <sup>1</sup>H NMR (200MHz, H<sub>2</sub>O) δ 6.83 (2H,s), 5.30 (2H,s), 4.43 (4H,s), 3.82 (3H, s).

4-methoxy-2,6-dichloromethylpyridine (5). This synthesis is carried out according literature.

25 N,N'-ditosyl-2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane. the procedure is similar to that described in the literature. The crude product obtained is practically pure (yield=95%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 250 MHz): 7.72 (4H, d, J= 7Hz), 7.4 (1H, t, J= 6Hz), 7.35 (4H, d, J= 7Hz), 7.1 (1H, d, J= 6Hz), 6.57 (2H, s), 4.45 (4H, s), 4.35 (4H, s), 3.65 (3H, s), 2.4 (6H, s).

- 5 2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane. The procedure is similar to the one described previously. The crude product obtained is purified by chromatography (alumina, CH<sub>2</sub>Cl<sub>2</sub>/MeOH 95:5), yield = 65%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 250 MHz): 7.15 (1H, t, J= 6Hz), 6.55 (1H, d, J= 6Hz), 6.05 (2H, s), 3.95 (4H, s), 3.87 (4H, s), 3.65 (3H, s).

- 10 Mass spectrum (EI): M<sup>+</sup> = 270 (100%)

**(ii) Synthesis of the complex [Fe(4OMeLN<sub>4</sub>H<sub>2</sub>)Cl<sub>2</sub>]Cl:**

- 270 mg of 2,11-diaza[3.3]-(4-methoxy)(2,6)pyridinophane (1 mmole) were dissolved in  
15 15 ml of dry THF. To this solution was added a solution of 270 mg of FeCl<sub>3</sub>·6H<sub>2</sub>O (1 mmole) in 5 ml of MeOH. The resulting mixture is evaporated to dryness and the solid product is dissolved in 10 ml of AcN with a minimum of MeOH. Slow diffusion of THF give 300 mg of brown crystals, yield = 70%. Elemental analysis for

C<sub>15</sub>H<sub>18</sub>N<sub>4</sub>Cl<sub>3</sub>OFe·0.5MeOH (found/theoretical): C=41.5/41.61 H=4.46/4.52

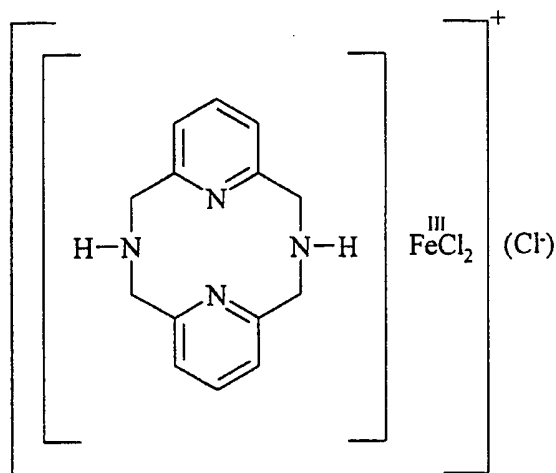
- 20 N=12.5/12.08

IR (KBr pellets, cm<sup>-1</sup>): 3545, 3414, 3235, 3075, 2883, 1615, 1477, 1437, 1340, 1157, 1049, 883, 628, 338.

**Example 5:**

25

This example describes a synthesis of a catalyst of formula (H) wherein:-



$R_1-R_8=\text{H}$ ;  $x=1$ ;  $y=1$ ;  $z=1$ ;  $\text{X}=\text{Cl}$ ,  $n=2$ ;  $\text{Y}=\text{Cl}^-$ ,  $p=1$

5

**Synthesis of the complex  $[\text{Fe}(\text{LN}_4\text{H}_2)\text{Cl}_2]\text{Cl}$ :**

240 mg of  $\text{LN}_4\text{H}_2$  (1 mmole) were dissolved in 15 ml of dry THF. To this solution was added a solution of 270 mg of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1 mmole) in 5 ml of MeOH. The resulting mixture is stirred and gives spontaneously 340 mg of yellow powder, yield = 85%. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3445, 3031, 2851, 1629, 1062, 1473, 1427, 1335, 1157, 1118, 1045, 936, 796, 340, 318

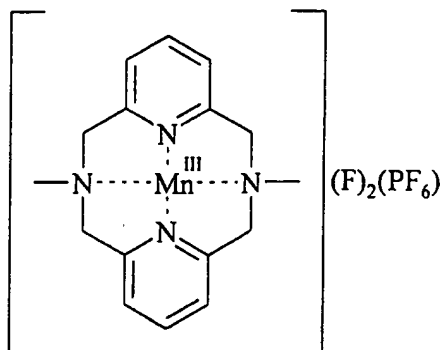
10

**Example 6:**

15

This Example describes a synthesis of a catalyst of formula (H) wherein:-





$R_1=R_2=R_{5-8}=H$ ;  $R_3=R_4=Me$ ;  $x=1$ ;  $y=1$ ;  $n=2$ ;  $z=1$ ;  $X=F^-$ ;  $m=2$ ;  $Y=PF_6^-$ ;  $p=1$

5

difluoro[N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane/manganese(III) hexafluorophosphate.

10 (i) Synthesis of the ligand N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane:

2,6-dichloromethylpyridine. A mixture of 2,6-dimethanolpyridine (5g, 36 mmol) and 75 ml of  $SOCl_2$  was refluxed for 4 hours. The mixture was concentrated (half volume). Toluene was added (50 ml). The solid formed after cooling was then filtered and dissolved in water and the solution neutralised with  $NaHCO_3$ . The solid obtained is filtered and dried (65%).  $^1H$  NMR (200MHz,  $CDCl_3$ )  $\delta$  7.8 (1H,t,  $J=7Hz$ ), 7.45 (2H,d,  $J=7 Hz$ ), 4.7 (4H, s).

Sodium p-toluenesulphonamidure. To a mixture of  $Na^+$  in dry EtOH (0.7 g, 29 mmol) was added p-toluenesulphonamide (5 g, 29 mmol) and the solution was refluxed for 2 hours. After cooling, the solid obtained was filtered, washed with EtOH and dried (quantitative yield).

N,N'-ditosyl-2,11-diaza[3.3](2,6)pyridinophane. To a solution of sodium p-toluenesulphonamidure (1.93 g, 10 mmol) in 200 ml of dry DMF at  $80^\circ C$  was slowly added 2,6-dichloromethylpyridine (1.76 g, 10 mmol). After 1 hour a new portion of

sodium *p*-toluenesulphonamidure was added (1.93 g) and the final mixture stirred at 80°C for an addition 4 hours. The solution was then evaporated to dryness. The solid obtained was washed with water and then with EtOH and finally crystallised in an CHCl<sub>3</sub>/MeOH mixture. The solid obtained is filtered and dried. The yield of (15) was 55 %. <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 7.78 (4H,d, J=6Hz), 7.45 (6H,m), 7.15 ( 4H,d, J=6Hz), 4.4 (8H, s), 2.4 (6H,s)

2,11-diaza[3.3](2,6)pyridinophane. A mixture of N,N'-ditosyl-2,11-diaza[3.3](2,6)pyridinophane (1.53 g, 2.8 mmoles) and 14 ml of H<sub>2</sub>SO<sub>4</sub> 90 % was heated at 110°C for 2 hours. The solution, cooled and diluted with 14 ml of water, was then carefully poured into a saturated NaOH solution. The solid formed is extracted with chloroform. The organic layer is evaporated to dryness to yield 85 % of 2,11-diaza[3.3](2,6)pyridinophane. <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 7.1 (2H,t, J=7Hz), 6.5 (4H,d, J=7 Hz), 3.9 (8H, s).

N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane. A mixture of 2,11-diaza[3.3](2,6)pyridinophane (0.57 g, 2.4 mmoles), 120 ml of formic acid and 32 ml of formaldehyde (32% in water) was refluxed for 24 hours. Concentrated HCl (10 ml) were added and the solution evaporated to dryness. The solid was dissolved in water and basified with NaOH 5M, and the resulting solution was extracted with CHCl<sub>3</sub>. The solid obtained was purified by chromatography on alox (CH<sub>2</sub>Cl<sub>2</sub>+1% MeOH) to yield 51 % of N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane. <sup>1</sup>H NMR (200MHz, CDCl<sub>3</sub>) δ 7.15 (2H,t, J=7Hz), 6.8 (4H,d, J=7 Hz), 3.9 (8H, s), 2.73 (6H,s).

25 (ii) Synthesis of the complex:

MnF<sub>3</sub> (41.8 mg, 373 mmoles) was dissolved in 5 ml of MeOH, and N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane (0.1 g, 373 mmoles) was added with 5 ml of THF. After 30 minutes of stirring at RT, 4 ml of THF saturated in NBu<sub>4</sub>PF<sub>6</sub> were added, and the solution left without stirring until the crystallisation was finished. The product was

collected by filtration to yield 80% of complex. Elemental analysis (found, theoretical):  
 %C (38.35, 37.94), %N (11.32, 11.1), %H (3.75, 3.95). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3086,  
 2965, 2930, 2821, 1607, 1478, 1444, 1425, 1174, 1034, 1019, 844, 796, 603, 574, 555.  
 UV-Vis ( $\text{CH}_3\text{CN}$ ,  $\lambda$  in nm,  $\epsilon$ ): 500, 110; 850, 30; ( $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ :1/1,  $\lambda$  in nm,  $\epsilon$ ): 465,  
 5 168; 850, 30.

#### **Example 7:**

Bleaching of tomato-oil stained cloths without and with addition of  
 $[\text{Fe}(\text{MeN4Py})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ , immediately after the wash ( $t=0$ ) and after 24 h storage  
 10 ( $t=1$  day).

In an aqueous solution containing 10 mM carbonate buffer (pH 10) without and with 0.6 g/l  
 LAS (linear alkylbenzene sulphonate) or containing 10 mM borate buffer (pH 8) without and  
 with 0.6 g/l LAS, tomato-soya oil stained cloths (6x6 cm) were added and stirred for 30  
 15 minutes at 30 °C. In a second series of experiments, the same tests were done in the  
 presence of 10  $\mu\text{M}$   $[\text{Fe}(\text{MeN4Py})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ , referred to in the table below as  
 Fe(MeN4Py).

After the wash, the cloths were dried in a tumble drier and the reflectance was measured with  
 20 a Minolta 3700d spectrophotometer at 460 nm. The difference in reflectance before and after  
 the wash is defined as  $\Delta R_{460}$  value.

The cloths were measured immediately after the wash ( $t=0$ ), and after 24 h storage in a dark  
 room under ambient conditions ( $t=1$ d). The results obtained are listed in the table below:

25

	$\Delta R$ value ( $t=0$ ) blank (no cat)	$\Delta R$ value ( $t=0$ ) + Fe(MeN4Py)	$\Delta R$ value ( $t=1$ d) blank	$\Delta R$ value ( $t=1$ d) + Fe(MeN4Py)
pH 8 no LAS	11.5	23	11.5	44
pH 8 with LAS	12.5	19	12.5	36

pH 10 no LAS	10.5	30	11.5	43
pH 10 with LAS	12.5	30	14	39

A clear bleaching effect can thus be observed after the treated fabric cloths were dried and stored.

**Example 8:**

- 5 Bleaching of tomato-oil stained cloths without and with addition of various metal catalysts measured after 24 hours storage in the dark under ambient conditions.

In an aqueous solution containing 10 mM carbonate buffer (pH 10) without and with 0.6 g/l LAS (linear alkylbenzene sulphonate) or containing 10 mM borate buffer (pH 8)  
 10 without and with 0.6 g/l LAS, tomato-soya oil stained cloths were added and kept in contact with the solution under agitation for 30 minutes at 30 °C. In comparative experiments, the same experiments were done by addition of 5 µM of dinuclear or 10 µM mononuclear complex, referred to in the table below.

- 15 After the wash, the cloths were rinsed with water and subsequently dried at 30 °C and the change in colour was measured after leaving the cloths for 24 h in the dark with a Linotype-Hell scanner (ex Linotype). The change in colour (including bleaching) is expressed as the  $\Delta E$  value. The measured colour difference ( $\Delta E$ ) between the washed cloth and the unwashed cloth is defined as follows:

20

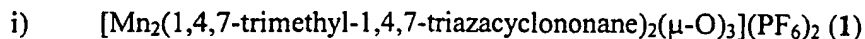
$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

- wherein  $\Delta L$  is a measure for the difference in darkness between the washed and unwashed test cloth;  $\Delta a$  and  $\Delta b$  are measures for the difference in redness and  
 25 yellowness respectively between both cloths. With regard to this colour measurement technique, reference is made to Commission International de l'Eclairage (CIE); Recommendation on Uniform Colour Spaces, colour difference equations, psychometric

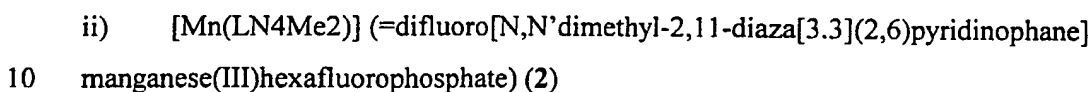
colour terms, supplement no 2 to CIE Publication, no 15, Colormetry, Bureau Central de la CIE, Paris 1978.

The following complexes were used:

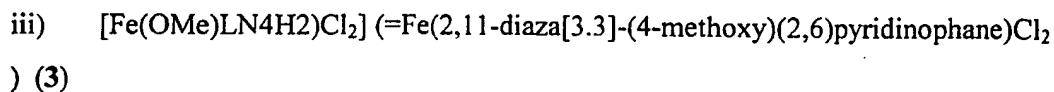
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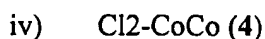
*Synthesised according to EP-B-458397;*



*Synthesised as described previously;*



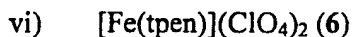
15 *Synthesised as described previously;*



*Synthesised according to EP-A-408131;*

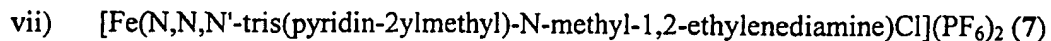


*Synthesised according to EP-A-408131;*



*Synthesised according to WO-A-9748787;*

25



*Synthesised according to I. Bernal, et al., J. Chem. Soc., Dalton Trans, 22, 3667 (1995);*

viii)  $[\text{Fe}_2(\text{N,N,N}'\text{-tetrakis}(\text{benzimidazol-2-ylmethyl})\text{-propan-2-ol-1,3-diamine})(\mu\text{-OH})(\text{NO}_3)_2](\text{NO}_3)_2$  (8)

*Synthesised according to Brennan, et al., Inorg. Chem., 30, 1937 (1991);*

5 ix)  $[\text{Mn}_2(\text{tpen})(\mu\text{-O})_2(\mu\text{-OAc})](\text{ClO}_4)_2$  (9)

*Synthesised according to Toftlund, H.; Markiewicz, A.; Murray, K.S.; Acta Chem. Scand., 44, 443 (1990);*

10 x)  $[\text{Mn}(\text{N,N,N}'\text{-tris}(\text{pyridin-2-ylmethyl})\text{-N'-methyl-1,2-ethylenediamine})\text{Cl}](\text{PF}_6)$  (10)

*Synthesised as follows:*

To a solution of manganese chloride tetrahydrate in tetrahydrofuran (0.190g, 1 mmol of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in 10 mL of THF) ligand trispicen(NMe) (0.347, 1 mmol) was added to give a brown precipitate (reference ligand: *I. Bernal, et al., J. Chem. Soc., Dalton Trans, 22, 3667 (1995)*). The mixture was stirred for 10 minutes and ammonium hexafluorophosphate (0.163g, 1 mmol) dissolved in THF was added to give a cream coloured precipitate. The mixture was filtered, the filtrate was washed with THF and dried under vacuum to furnish the complex ( $\text{FW}=522.21\text{g}\cdot\text{mol}^{-1}$ ) as a white solid (0.499g, 86%). ESMS ( $m/z$ ): 437 ( $[\text{LMnCl}]^+$ )

20

xi)  $[\text{Mn}_2(\text{N,N}'\text{-bis}(\text{pyridin-2-ylmethyl})\text{-1,2-ethylenediamine})_2(\mu\text{-O})_2](\text{ClO}_4)_3$  (11)

*Synthesised according to Glerup, J.; Goodson, P. A.; Hazell, A.; Hazell, R.; Hodgson, D. J.; McKenzie, C. J.; Michelsen, K.; Rychlewska, U.; Toftlund, H. Inorg. Chem. (1994), 33(18), 4105-11;*

25

xii)  $[\text{Mn}(\text{N,N}'\text{-bis}(\text{pyridin-2-ylmethyl})\text{-N,N}'\text{-dimethyl-1,2-ethylenediamine})_2\text{Cl}_2]$  (12)

*Synthesised as follows:*

Triethylamine (0.405g, 4 mmol) was a solution of salt of the ligand bispicen(NMe) (0.416g, 1 mmol) in tetrahydrofuran anhydrous (10 mL) (ref ligand: C. Li, et al, J. Chem. Soc., Dalton Trans. (1991), 1909-14). The mixture was stirred at

30

room temperature for 30 minutes. A few drops of methanol were added. The mixture was filtered. Manganese chloride (0.198g, 1 mmol) dissolved in THF (1 mL) was added to the mixture to give, after a stirring of 30 minutes, a white precipitate. The solution was filtered, the filtrate was washed twice with dry ether and dried under vacuum. This  
5 gave 0.093g of complex (23% yield).

xiii)  $[\text{Mn}_2(\text{N},\text{N},\text{N}',\text{N}'\text{-tetrakis(pyridin-2-ylmethyl)-propan-1,3-diamine})(\mu\text{-O})(\mu\text{-OAc})_2](\text{ClO}_4)_2$  (13)

*Synthesised as follows:*

10 To a stirred solution of 6.56 g 2-chloro-methylpyridine (40 mmol) and 0.75 ml 1,3-propanediamine (9 mmol) in 40 ml water, is added slowly at 70°C over a period of 10 minutes, 8 ml 10M NaOH-solution. The colour of the reaction turned from yellow to deep red. The reaction was stirred for an additional 30 minutes at 70°C, after which the reaction was cooled to room temperature. The reaction mixture was extracted with  
15 dichloromethane (totally 200 ml), after which the red organic layer was dried over  $\text{MgSO}_4$ , filtered and evaporated under reduced pressure, to yield 4.51 g of a red/brown oil. After scratching the bottom with a spatula the residue turned solid, trying to purify the crude product by washing it with water the product became messy, so immediately the purification was stopped and dried with ether. A sample was taken to analyse the  
20 product by NMR, while the rest was immediately reacted with  $\text{Mn}(\text{OAc})_3$  (see complexation).

$^1\text{H-NMR}$  (400MHz) ( $\text{CDCl}_3$ );  $\delta$  (ppm): 1.65 (q-5, propane-A, 2H), 2.40 (t, propane-B, 4H), 3.60 (s, N- $\text{CH}_2$ -pyr, 8H), 6.95 (t, pyr-H4, 4H), 7.30 (d, pyr-H3, 4H), 7.45 (t, pyr-H5, 4H), 8.35 (d, pyr-H6, 4H).

25 To a stirred solution of 4.51 g TPTN (0.0103 mol) in 40 ml methanol is added at room temperature (22°C) 2.76 g  $\text{Mn}(\text{OAc})_3$  (0.0103 mol). The colour of the reaction turned from orange to dark brown, after the addition the mixture was stirred for 30 minutes at room temperature and filtered. To the filtrate was added at room temperature 1.44 g  $\text{NaClO}_4$  (0.0103 mmol) and the reaction mixture was stirred for another hour,  
30 filtered and nitrogen dried, yielding 0.73 g bright brown crystals (8%).

$^1\text{H-NMR}$  (400MHz) ( $\text{CD}_3\text{CN}$ );  $\delta$  (ppm): -42.66 (s), -15.43 (s), -4.8 (s, br.), 0-10 (m, br.), 13.81 (s), 45.82 (s), 49.28 (s), 60 (s, br.), 79 (s, br.), 96 (s, br.)

IR/ ( $\text{cm}^{-1}$ ): 3426, 1608 (C=C), 1563 (C=N), 1487, 1430 (C-H), 1090 ( $\text{ClO}_4$ ), 1030, 767, 623.

- 5 UV/Vis ( $\lambda$ , nm( $\epsilon$ ,  $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ): 260 ( $2.4 \times 10^4$ ), 290 (sh), 370 (sh), 490 ( $5.1 \times 10^2$ ), 530 (sh;  $3.4 \times 10^2$ ), 567 (sh), 715 ( $1.4 \times 10^2$ ).

Mass spectrum: (ESP+)  $m/z$  782 [ $\text{TPTN Mn(II)Mn(III) } (\mu\text{-OH}) (\mu\text{-OAc})_2 (\text{ClO}_4)^+]$

ESR ( $\text{CH}_3\text{CN}$ ): The complex is ESR silent supporting the presence of a  $\text{Mn(III)Mn(III)}$  species.

- 10 Elemental analysis: found (expected for  $\text{Mn}_2\text{C}_{31}\text{H}_{38}\text{N}_6\text{O}_{14}\text{Cl}_2$  (MW=899): C 41.14 (41.4), H 4.1 (4.2), N 9.23 (9.34), O 24.8 (24.9), Cl 7.72 (7.9), Mn 12.1 (12.2).

xiv)  $[\text{Mn}_2(\text{tpa})_2(\mu\text{-O})_2](\text{PF}_6)_3$  (14)

*Synthesised according to D.K. Towle, C.A. Botsford, D.J. Hodgson, ICA, 141,*

- 15 *167 (1988);*

xv)  $[\text{Fe}(\text{N4Py})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$  (15)

*Synthesised according to WO-A-9534628;*

- 20 xvi)  $[\text{Fe}(\text{MeN4Py})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$  (16)

*Synthesised according to EP-A-0909809.*

xvii)  $[\text{Mn}_2(2,6\text{-bis}\{(\text{bis}(2\text{-pyridylmethyl})\text{amino})\text{methyl}\}\text{-4-methylphenol})(\mu\text{-OAc})_2](\text{ClO}_4)_2$  (17)

- 25 *Synthesised according to H. Diril et al., J.Am.Chem.Soc., 111, 5102 (1989);*

xviii)  $[\text{Mn}_2(\text{N,N,N',N'}$ -tetrakis(benzimidazol-2-ylmethyl)-propan-2-olate-1,3-diamine)]  
( $\mu\text{-OAc})_2](\text{ClO}_4)_2$  (18)

*Synthesised according to P. Marthur et al., J.Am.Chem.Soc., 109, 5227 (1987).*



Results:

- 5 Table: bleach activity on Tomato Oil stains expressed in  $\Delta E$  values obtained for various metal complexes measured after 24 h.

	BL *	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	16 **
pH 8 -LAS	1	1	2	2	4	9	2	9	4	2	7	2	2	2	6	20	19	2	1	21
pH 8 +LAS	2	6	7	7	2	6	19	19	2	18	10	18	5	7	6	20	20	3	2	23
pH10 -LAS	1	1	3	3	9	17	2	4	9	2	2	4	2	5	4	19	18	3	8	21
pH10 +LAS	3	16	14	14	4	11	6	11	4	4	4	16	17	7	7	19	20	11	5	21

\* BL: Reference: no catalyst added, only buffer with and without LAS

10 \*\* Compound 16 with 10 mM hydrogen peroxide

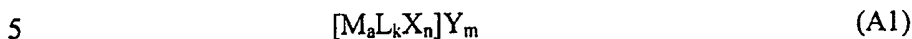
Performing the experiment under argon (compound 16 at pH 10 with LAS) showed that the bleaching effect upon storage is absent, thus showing that dioxygen is involved in the bleaching process.

**CLAIMS:**

1. A method of treating a textile by contacting the textile with an organic substance which forms a complex with a transition metal, whereby the complex catalyses  
5 bleaching of the textile by atmospheric oxygen after the treatment.
2. A method according to claim 1, wherein the treatment comprises contacting the textile with the organic substance in dry form.
- 10 3. A method according to claim 1, wherein the treatment comprises contacting the textile with a liquor containing the organic substance and then drying.
4. A method according to claim 3, wherein the liquor is an aqueous liquor.
- 15 5. A method according to claim 4, wherein the liquor is a spray-on fabric treatment fluid.
6. A method according to claim 4, wherein the liquor is a wash liquor for laundry cleaning.  
20
7. A method according to claim 3, wherein the liquor is a non-aqueous liquor.
8. A method according to claim 7, wherein the liquor is a dry cleaning fluid.
- 25 9. A method according to claim 7, wherein the liquor is a spray-on aerosol fluid.
10. A method according to any of claims 3 to 9, wherein the liquor is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

11. A method according to claim 3, wherein the medium has a pH value in the range from pH 6 to 11.
12. A method according to claim 11, wherein the liquor has a pH value in the range  
5 from pH 8 to 10.
13. A method according to any of claims 3 to 12, wherein the liquor is substantially devoid of a transition metal sequestrant.
- 10 14. A method according to any of claims 3 to 13, wherein the liquor further comprises a surfactant.
15. A method according to any of claims 3 to 14, wherein the liquor further comprises a builder.  
15
16. A method according to any preceding claim, wherein the treated textile is dried and bleaching is catalysed on the dry textile.
17. A method according to any of claims 1 to 16, wherein the organic substance  
20 comprises a preformed complex of a ligand and a transition metal.
18. A method according to any of claims 3 to 16, wherein the organic substance comprises a free ligand that complexes with a transition metal present in the liquor.
- 25 19. A method according to any of claims 1 to 16, wherein the organic substance comprises a free ligand that complexes with a transition metal present in the textile.
20. A method according to any of claims 1 to 16, wherein the organic substance comprises a composition of a free ligand or a transition metal-substitutable metal-ligand  
30 complex, and a source of transition metal.

21. A method according to any of claims 1 to 20, wherein the organic substance forms a complex of the general formula (A1):



in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(I)-(II)-(III)-(IV), Co(I)-(II)-(III), Ni(I)-(II)-(III), Cr(II)-(III)-(IV)-(V)-(VI)-(VII), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI), W(IV)-(V)-(VI), Pd(II), Ru(II)-(III)-(IV)-(V) and Ag(I)-(II);

L represents a ligand, or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

a represents an integer from 1 to 10;

k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 10; and

20 m represents zero or an integer from 1 to 20.

22. A method according to claim 21, wherein in formula (A1):

X represents a coordinating species selected from  $O^{2-}$ ,  $RBO_2^{2-}$ ,  $RCOO^-$ ,  $RCONR^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $NO$ ,  $CO$ ,  $S^{2-}$ ,  $RS^-$ ,  $PO_3^{4-}$ , STP-derived anions,  $PO_3OR^{3-}$ ,  $H_2O$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $ROH$ ,  $NRR'R''$ ,  $RCN$ ,  $Cl^-$ ,  $Br^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $CN^-$ ,  $N_3^-$ ,  $F^-$ ,  $I^-$ ,  $RO^-$ ,  $ClO_4^-$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$  and  $RSO_3^-$ ; and

Y represents a counter ion selected from  $ClO_4^-$ ,  $BR_4^-$ ,  $[FeCl_4]^-$ ,  $PF_6^-$ ,  $RCOO^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $RO^-$ ,  $N^+RR'R''R'''$ ,  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $I^-$ ,  $RSO_3^-$ ,  $S_2O_6^{2-}$ ,  $OCN^-$ ,  $SCN^-$ ,  $Li^+$ ,  $Ba^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Cs^+$ ,  $PR_4^+$ ,  $RBO_2^{2-}$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$ ,  $SbCl_6^-$ ,  $CuCl_4^{2-}$ ,  $CN$ ,  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$ , STP-derived anions,  $CO_3^{2-}$ ,  $HCO_3^-$  and  $BF_4^-$ , wherein

R, R', R'', R''' independently represent a group selected from hydrogen, hydroxyl, -OR (wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or carbonyl derivative group), -OAr, alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups, each of R, Ar, alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups being optionally substituted by one or more functional groups E, or R6 together with R7 and independently R8 together with R9 represent oxygen;

E is selected from functional groups containing oxygen, sulphur, phosphorus, nitrogen, selenium, halogens, and any electron donating and/or withdrawing groups.

10

23. A method according to claim 21 or claim 22, wherein in formula (A1):

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II), Fe(II)-(III)-(IV) and Co(I)-(II)-(III);

X represents a coordinating species selected from  $O^{2-}$ ,  $RBO_2^{2-}$ ,  $RCOO^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $NO$ ,  $CO$ ,  $CN^-$ ,  $S^{2-}$ ,  $RS^-$ ,  $PO_3^{4-}$ ,  $H_2O$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $ROH$ ,  $NRR'R''$ ,  $Cl^-$ ,  $Br^-$ ,  $OCN^-$ ,  $SCN^-$ ,  $RCN$ ,  $N_3^-$ ,  $F^-$ ,  $I^-$ ,  $RO^-$ ,  $ClO_4^-$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$  and  $RSO_3^-$ ;

Y represents a counter ion selected from  $ClO_4^-$ ,  $BR_4^-$ ,  $[FeCl_4]^-$ ,  $PF_6^-$ ,  $RCOO^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $RO^-$ ,  $N^+RR'R''R'''$ ,  $Cl^-$ ,  $Br^-$ ,  $F^-$ ,  $I^-$ ,  $RSO_3^-$ ,  $S_2O_6^{2-}$ ,  $OCN^-$ ,  $SCN^-$ ,  $Li^+$ ,  $Ba^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $PR_4^+$ ,  $SO_4^{2-}$ ,  $HSO_4^-$ ,  $SO_3^{2-}$  and  $BF_4^-$ , wherein

20 R, R', R'', R''' represent represent hydrogen, optionally substituted alkyl or optionally substituted aryl;

a represents an integer from 1 to 4;

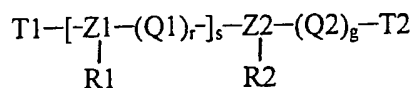
k represents an integer from 1 to 10;

n represents zero or an integer from 1 to 4; and

25 m represents zero or an integer from 1 to 8.

24. A method according to any of claims 21 to 23, wherein L represents a ligand of the general formula (BI):

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wherein

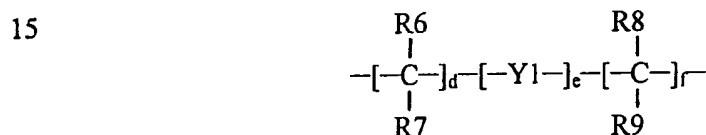
5 g represents zero or an integer from 1 to 6;

r represents an integer from 1 to 6;

s represents zero or an integer from 1 to 6;

10 Z1 and Z2 independently represent a heteroatom or a heterocyclic or heteroaromatic ring, Z1 and/or Z2 being optionally substituted by one or more functional groups E as defined below;

Q1 and Q2 independently represent a group of the formula:



wherein

20  $10 > d+e+f > 1$ ;  $d=0-9$ ;  $e=0-9$ ;  $f=0-9$ ;

each Y1 is independently selected from -O-, -S-, -SO-, -SO<sub>2</sub>-, -(G<sup>1</sup>)N-, -(G<sup>1</sup>)(G<sup>2</sup>)N- (wherein G<sup>1</sup> and G<sup>2</sup> are as defined below), -C(O)-, arylene, alkylene, heteroarylene, -P- and -P(O)-;

25 if  $s > 1$ , each -[Z1(R1)-(Q1)<sub>r</sub>]- group is independently defined;

R1, R2, R6, R7, R8, R9 independently represent a group selected from hydrogen, hydroxyl, -OR (wherein R= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or carbonyl derivative group), -OAr, alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups, each of R, Ar, alkyl,

30

alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl and carbonyl derivative groups being optionally substituted by one or more functional groups E, or R6 together with R7 and independently R8 together with R9 represent oxygen;

E is selected from functional groups containing oxygen, sulphur, phosphorus,  
 5 nitrogen, selenium, halogens, and any electron donating and/or withdrawing groups (preferably E is selected from hydroxy, mono- or polycarboxylate derivatives, aryl, heteroaryl, sulphonate, thiol (-RSH), thioethers (-R-S-R'), disulphides (-RSSR'), dithiolenes, mono- or polyphosphonates, mono- or polyphosphates, electron donating groups and electron withdrawing groups, and groups of formulae  $(G^1)(G^2)N-$ ,  $(G^1)(G^2)$   
 10  $(G^3)N-$ ,  $(G^1)(G^2)N-C(O)-$ ,  $G^3O-$  and  $G^3C(O)-$ , wherein each of  $G^1$ ,  $G^2$  and  $G^3$  is independently selected from hydrogen, alkyl, electron donating groups and electron withdrawing groups (in addition to any amongst the foregoing));

or one of R1-R9 is a bridging group bound to another moiety of the same general formula;

15

T1 and T2 independently represent groups R4 and R5, wherein R4 and R5 are as defined for R1-R9, and if  $g=0$  and  $s>0$ , R1 together with R4, and/or R2 together with R5, may optionally independently represent  $=CH-R_{10}$ , wherein R10 is as defined for R1-R9, or

20 T1 and T2 may together (-T2-T1-) represent a covalent bond linkage when  $s>1$  and  $g>0$ ;

if Z1 and/or Z2 represent N and T1 and T2 together represent a single bond linkage and R1 and/or R2 are absent, Q1 and/or Q2 may independently represent a  
 25 group of the formula:  $=CH-[-Y1-]_e-CH=$ ,

optionally any two or more of R1, R2, R6, R7, R8, R9 independently are linked together by a covalent bond;

30 if Z1 and/or Z2 represents O, then R1 and/or R2 do not exist;

if Z1 and/or Z2 represents S, N, P, B or Si then R1 and/or R2 may be absent;

if Z1 and/or Z2 represents a heteroatom substituted by a functional group E then R1 and/or R2 and/or R4 and/or R5 may be absent.

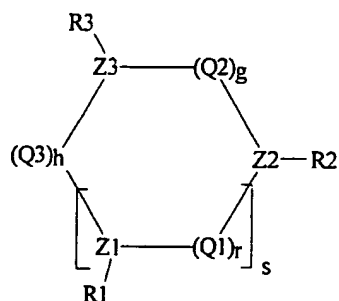
- 5 25. A method according to claim 24, wherein Z1 and Z2 independently represent an optionally substituted heteroatom selected from N, P, O, S, B and Si or an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidines, pyrazine, pyrimidine, pyrazole, pyrrole, imidazole, benzimidazole, quinoline, isoquinoline, carbazole, indole, isoindole, furane, thiophene, 10 oxazole and thiazole.

26. A method according to claim 24 or claim 25, wherein R1-R9 are independently selected from -H, hydroxy-C<sub>0</sub>-C<sub>20</sub>-alkyl, halo-C<sub>0</sub>-C<sub>20</sub>-alkyl, nitroso, formyl-C<sub>0</sub>-C<sub>20</sub>-alkyl, carboxyl-C<sub>0</sub>-C<sub>20</sub>-alkyl and esters and salts thereof, carbamoyl-C<sub>0</sub>-C<sub>20</sub>-alkyl, sulpho-C<sub>0</sub>-C<sub>20</sub>-alkyl and esters and salts thereof, sulphonamoyl-C<sub>0</sub>-C<sub>20</sub>-alkyl, amino-C<sub>0</sub>-C<sub>20</sub>-alkyl, 15 aryl-C<sub>0</sub>-C<sub>20</sub>-alkyl, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyl, C<sub>0</sub>-C<sub>20</sub>-alkyl, alkoxy-C<sub>0</sub>-C<sub>8</sub>-alkyl, carbonyl-C<sub>0</sub>-C<sub>6</sub>-alkoxy, and aryl-C<sub>0</sub>-C<sub>6</sub>-alkyl and C<sub>0</sub>-C<sub>20</sub>-alkylamide;

- or one of R1-R9 is a bridging group -C<sub>n</sub>-(R11)(R12)-(D)<sub>p</sub>-C<sub>m</sub>-(R11)(R12)- bound to another moiety of the same general formula, wherein p is zero or one, D is selected 20 from a heteroatom or a heteroatom-containing group, or is part of an aromatic or saturated homonuclear and heteronuclear ring, n' is an integer from 1 to 4, m' is an integer from 1 to 4, with the proviso that n'+m'≤4, R11 and R12 are each independently preferably selected from -H, NR13 and OR14, alkyl, aryl, optionally substituted, and R13 and R14 are each independently selected from -H, alkyl, aryl, both 25 optionally substituted.

27. A method according to any of claims 24 to 26, wherein T1 and T2 together form a single bond linkage and s>1, according to general formula (BII):





wherein Z3 independently represents a group as defined for Z1 or Z2; R3 independently represents a group as defined for R1-R9; Q3 independently represents a group as defined for Q1, Q2; h represents zero or an integer from 1 to 6; and  $s'=s-1$ .

5

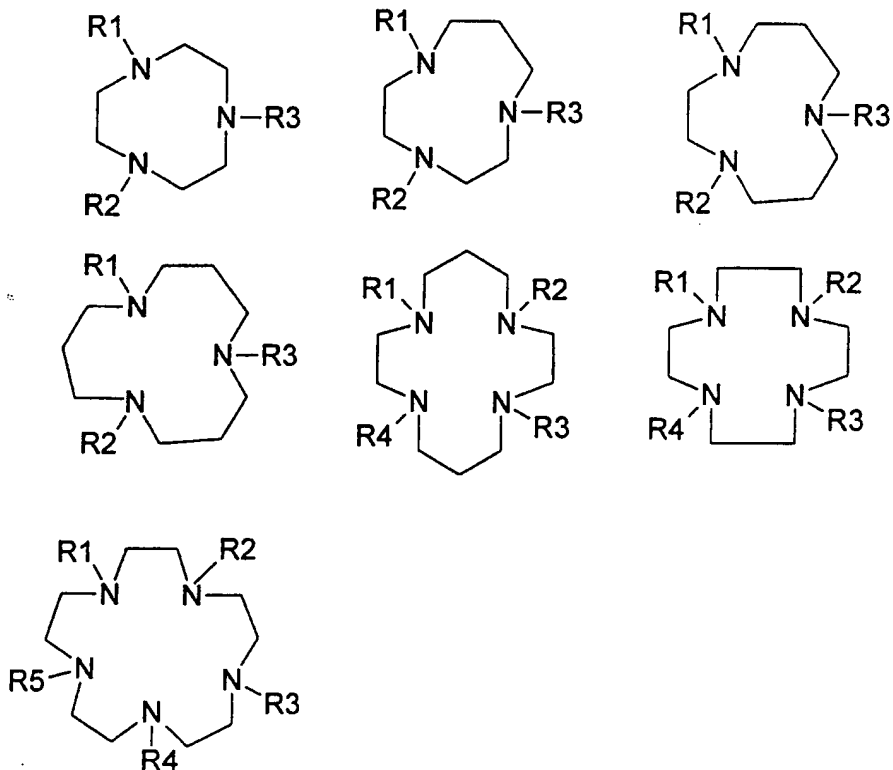
28. A method according to claim 27, wherein in general formula (BII),  $s'=1, 2$  or  $3$ ;  $r=g=h=1$ ;  $d=2$  or  $3$ ;  $e=f=0$ ;  $R6=R7=H$ .

29. A method according to claim 28, wherein the ligand has a general formula selected from:

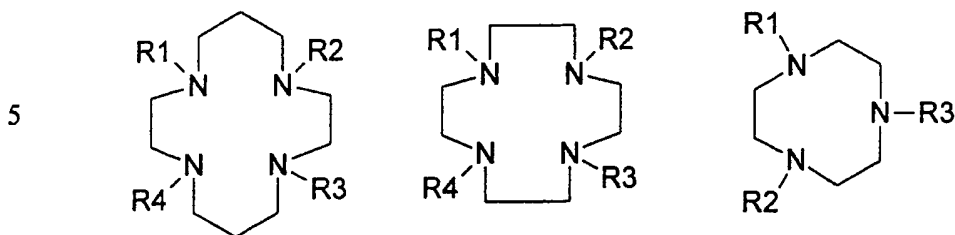
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30. A method according to claim 29, wherein the ligand has a general formula selected from:



31. A method according to claim 30, wherein R1, R2, R3 and R4 are independently selected from -H, alkyl, heteroaryl, or represents a bridging group bound to another moiety of the same general formula with the bridging group being alkylene or hydroxy-alkylene or a heteroaryl-containing bridge.

10

32. A method according to claim 31, wherein R1, R2, R3 and R4 are independently selected from -H, methyl, ethyl, isopropyl, nitrogen-containing heteroaryl, or a bridging group bound to another moiety of the same general formula with the bridging group being alkylene or hydroxy-alkylene.

15

33. A method according to any of claims 28 to 32, wherein in the complex

20

$$[M_a L_k X_n] Y_m :$$

M = Mn(II)-(IV), Cu(I)-(III), Fe(II)-(III), Co(II)-(III);

X = CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>,

RCOO<sup>-</sup>;

Y = ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>

25 a = 1, 2, 3, 4;

n = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;

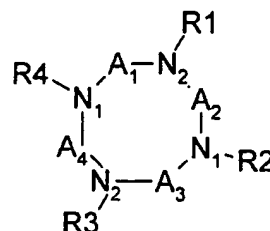
m = 1, 2, 3, 4; and

k = 1, 2, 4.

34. A method according to claim 27, wherein in general formula (BII),  $s'=2$ ;  $r=g=h=1$ ;  $d=f=0$ ;  $e=1$ ; and each Y1 is independently alkylene or heteroarylene.

35. A method according to claim 34, wherein the ligand has the general formula:

5



wherein

$A_1, A_2, A_3, A_4$  are independently selected from  $C_{1-9}$ -alkylene or heteroarylene groups; and

10  $N_1$  and  $N_2$  independently represent a hetero atom or a heteroarylene group.

36. A bleaching composition according to claim 35, wherein

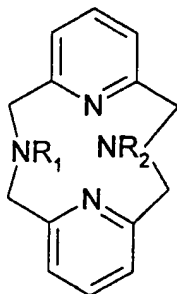
$N_1$  represents an aliphatic nitrogen;

$N_2$  represents a heteroarylene group;

15  $R_1, R_2, R_3, R_4$  each independently represent -H, alkyl, aryl or heteroaryl; and  $A_1, A_2, A_3, A_4$  each represent  $-CH_2-$ .

37. A method according to claim 36, wherein the ligand has the general formula:

20



25

wherein  $R_1, R_2$  each independently represent -H, alkyl, aryl or heteroaryl.

38. A method according to any of claims 34 to 37, wherein in the complex



M= Fe(II)-(III), Mn(II)-(IV), Cu(II), Co(II)-(III);

X= CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>,

5 RCOO<sup>-</sup>;

Y= ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>;

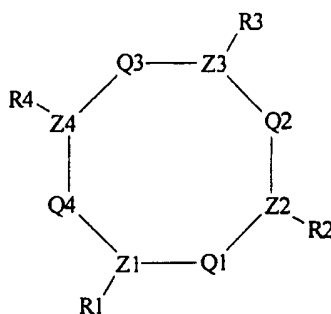
a= 1, 2, 3, 4;

n= 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;

m= 1, 2, 3, 4; and

10 k= 1, 2, 4.

39. A method according to claim 27, wherein in general formula (BII), s'=2 and r=g=h=1, according to the general formula:

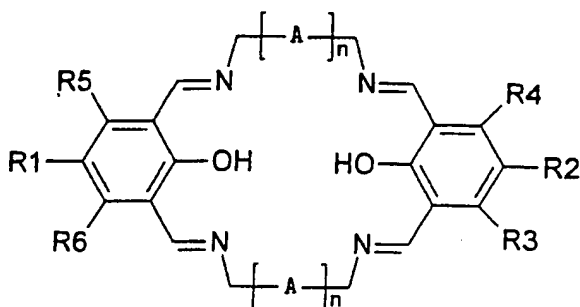


15

40. A method according to claim 39, wherein Z1=Z2=Z3=Z4=a heteroaromatic ring; e=f=0; d=1; and R7 is absent.

20 41. A method according to claim 39, wherein Z1-Z4 each represent N; R1-R4 are absent; both Q1 and Q3 represent =CH-[Y1]<sub>e</sub>-CH= ; and both Q2 and Q4 represent -CH<sub>2</sub>-[Y1]<sub>n</sub>-CH<sub>2</sub>-.

25 42. A method according to claim 41, wherein the ligand has the general formula:



wherein A represents optionally substituted alkylene optionally interrupted by a heteroatom; and n is zero or an integer from 1 to 5.

5 43. A method according to claim 42 wherein R1-R6 represent hydrogen, n=1 and A = -CH<sub>2</sub>-, -CHOH-, -CH<sub>2</sub>N(R)CH<sub>2</sub>- or -CH<sub>2</sub>CH<sub>2</sub>N(R)CH<sub>2</sub>CH<sub>2</sub>- wherein R represents hydrogen or alkyl.

44. A method according to claim 43, wherein A = -CH<sub>2</sub>-, -CHOH- or -  
10 CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>-.

45. A method according to any of claims 39 to 44 wherein in the complex  
[M<sub>a</sub>L<sub>k</sub>X<sub>n</sub>]Y<sub>m</sub>:

M = Mn(II)-(IV), Co(II)-(III), Fe(II)-(III);

15 X = CH<sub>3</sub>CN, OH<sub>2</sub>, Cl<sup>-</sup>, Br<sup>-</sup>, OCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, OH<sup>-</sup>, O<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, C<sub>6</sub>H<sub>5</sub>BO<sub>2</sub><sup>2-</sup>,  
RCOO<sup>-</sup>;

Y = ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, [FeCl<sub>4</sub>]<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>;

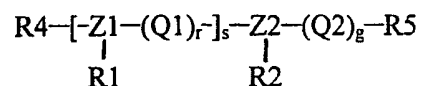
a = 1, 2, 3, 4;

$n = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;$

$m = 1, 2, 3, 4;$  and

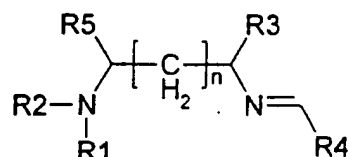
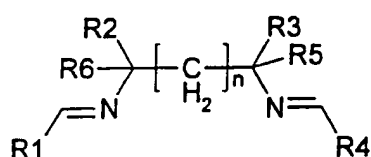
$k = 1, 2, 4.$

- 5 46. A method according to any of claims 24 to 26, wherein T1 and T2 independently represent groups R4, R5 as defined for R1-R9, according to the general formula (BIII):



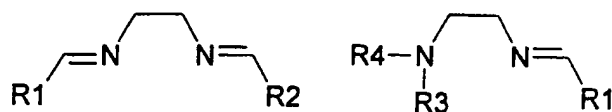
10

47. A method according to claim 46, wherein in general formula (BIII),  $s=1$ ;  $r=1$ ;  $g=0$ ;  $d=f=1$ ;  $e=1-4$ ;  $\text{Y1} = -\text{CH}_2-$ ; and R1 together with R4, and/or R2 together with R5, independently represent  $=\text{CH-R10}$ , wherein R10 is as defined for R1-R9.
- 15 48. A method according to claim 47, wherein R2 together with R5 represents  $=\text{CH-R10}$ .
49. A method according to claim 47 or claim 48, wherein the ligand is selected from:



50. A method according to claim 49, wherein the ligand is selected from:

5



wherein R1 and R2 are selected from optionally substituted phenols, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, heteroaryl-C<sub>0</sub>-C<sub>20</sub>-alkyls, alkylaryl, aminoalkyl, alkoxy.

51. A method according to claim 50 wherein R1 and R2 are selected from optionally substituted phenols, heteroaryl-C<sub>0</sub>-C<sub>2</sub>-alkyls, R3 and R4 are selected from -H, alkyl, aryl, optionally substituted phenols, nitrogen-heteroaryl-C<sub>0</sub>-C<sub>2</sub>-alkyls.

52. A method according to any of claims 47 to 51 wherein in the complex [M<sub>a</sub>L<sub>k</sub>X<sub>n</sub>]Y<sub>m</sub>:

M = Mn(II)-(IV), Co(II)-(III), Fe(II)-(III);

$X = \text{CH}_3\text{CN}, \text{OH}_2, \text{Cl}^-, \text{Br}^-, \text{OCN}^-, \text{N}_3^-, \text{SCN}^-, \text{OH}^-, \text{O}^{2-}, \text{PO}_4^{3-}, \text{C}_6\text{H}_5\text{BO}_2^{2-},$

$\text{RCOO}^-;$

$Y = \text{ClO}_4^-, \text{BPh}_4^-, \text{Br}^-, \text{Cl}^-, [\text{FeCl}_4]^-, \text{PF}_6^-, \text{NO}_3^-;$

$a = 1, 2, 3, 4;$

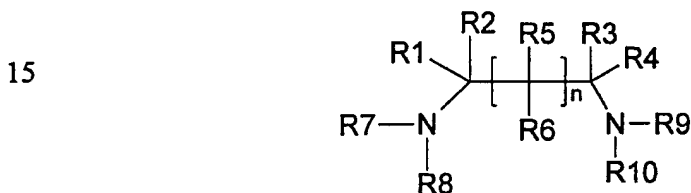
5  $n = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9;$

$m = 1, 2, 3, 4;$  and

$k = 1, 2, 4.$

53. A bleaching composition according to claim 46, wherein in general formula  
10 (BIII),  $s=1; r=1; g=0; d=f=1; e=1-4; Y1 = -C(R')(R'')$ , wherein  $R'$  and  $R''$  are independently as defined for  $R1-R9$ .

54. A method according to claim 53, wherein the ligand has the general formula:



55. A method according to claim 54, wherein  $R1, R2, R3, R4, R5$  are  $-H$  or  $C_0-C_{20}$ -  
20 alkyl,  $n=0$  or  $1$ ,  $R6$  is  $-H$ , alkyl,  $-OH$  or  $-SH$ , and  $R7, R8, R9, R10$  are each independently selected from  $-H$ ,  $C_0-C_{20}$ -alkyl, heteroaryl- $C_0-C_{20}$ -alkyl, alkoxy- $C_0-C_8$ -alkyl and amino- $C_0-C_{20}$ -alkyl.

56. A method according to any of claims 53 to 55 wherein in the complex  
25  $[\text{M}_a\text{L}_k\text{X}_n]\text{Y}_m:$

$\text{M} = \text{Mn(II)-(IV)}, \text{Fe(II)-(III)}, \text{Cu(II)}, \text{Co(II)-(III)};$

$X = \text{CH}_3\text{CN}, \text{OH}_2, \text{Cl}^-, \text{Br}^-, \text{OCN}^-, \text{N}_3^-, \text{SCN}^-, \text{OH}^-, \text{O}^{2-}, \text{PO}_4^{3-}, \text{C}_6\text{H}_5\text{BO}_2^{2-},$

$\text{RCOO}^-;$

$Y = \text{ClO}_4^-, \text{BPh}_4^-, \text{Br}^-, \text{Cl}^-, [\text{FeCl}_4]^-, \text{PF}_6^-, \text{NO}_3^-;$

30  $a = 1, 2, 3, 4;$



$n = 0, 1, 2, 3, 4;$

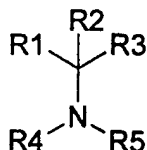
$m = 0, 1, 2, 3, 4, 5, 6, 7, 8;$  and

$k = 1, 2, 3, 4.$

- 5 57. A method according to claim 46, wherein in general formula (BIII),  $s=0$ ;  $g=1$ ;  $d=e=0$ ;  $f=1-4$ .

58. A method according to claim 57, wherein the ligand has the general formula:

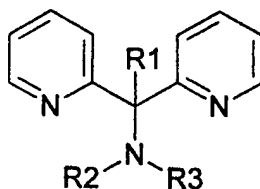
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59. A method according to claim 58, with the proviso that none of R1 to R3 represents hydrogen.

15

60. A method according to claim 58 or claim 59, wherein the ligand has the general formula:



20

wherein R1, R2, R3 are as defined for R2, R4, R5.

61. A method according to any of claims 57 to 60, wherein in the complex  $[M_a L_k X_n] Y_m$ :

25  $M = \text{Mn(II)-(IV)}, \text{Fe(II)-(III)}, \text{Cu(II)}, \text{Co(II)-(III)};$

$X = \text{CH}_3\text{CN}, \text{OH}_2, \text{Cl}^-, \text{Br}^-, \text{OCN}^-, \text{N}_3^-, \text{SCN}^-, \text{OH}^-, \text{O}^{2-}, \text{PO}_4^{3-}, \text{C}_6\text{H}_5\text{BO}_2^{2-}, \text{RCOO}^-;$

$Y = \text{ClO}_4^-, \text{BPh}_4^-, \text{Br}^-, \text{Cl}^-, [\text{FeCl}_4]^-, \text{PF}_6^-, \text{NO}_3^-;$

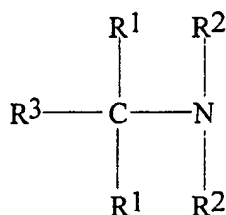
$a = 1, 2, 3, 4;$

$n = 0, 1, 2, 3, 4;$

$m = 0, 1, 2, 3, 4, 5, 6, 7, 8;$  and

5  $k = 1, 2, 3, 4.$

62. A method according to any of claims 21 to 26, wherein L represents a pentadentate ligand of the general formula (B):



10 wherein

each  $\text{R}^1, \text{R}^2$  independently represents  $-\text{R}^4-\text{R}^5$ ,

$\text{R}^3$  represents hydrogen, optionally substituted alkyl, aryl or arylalkyl, or  $-\text{R}^4-\text{R}^5$ ,

each  $\text{R}^4$  independently represents a single bond or optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene, alkylene ether, carboxylic ester or

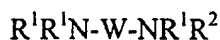
15 carboxylic amide, and

each  $\text{R}^5$  independently represents an optionally N-substituted aminoalkyl group or an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl.

20 63. A method according to claim 62, with the proviso that  $\text{R}^3$  does not represent hydrogen.

64. A method according to any of claims 21 to 26, wherein L represents a pentadentate or hexadentate ligand of the general formula (C):

25



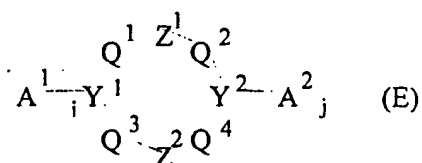
wherein

each  $R^1$  independently represents  $-R^3-V$ , in which  $R^3$  represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and  $V$  represents an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;

$W$  represents an optionally substituted alkylene bridging group selected from  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$ ,  $-CH_2-C_6H_4-CH_2-$ ,  $-CH_2-C_6H_{10}-CH_2-$ , and  $-CH_2-C_{10}H_6-CH_2-$ ; and

$R^2$  represents a group selected from  $R^1$ , and alkyl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulphonate, amine, alkylamine and  $N^+(R^4)_3$ , wherein  $R^4$  is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

65. A method according to any of claims 21 to 26, wherein  $L$  represents a macrocyclic ligand of formula (E):



wherein

$Z^1$  and  $Z^2$  are independently selected from monocyclic or polycyclic aromatic ring structures optionally containing one or more heteroatoms, each aromatic ring structure being substituted by one or more substituents;

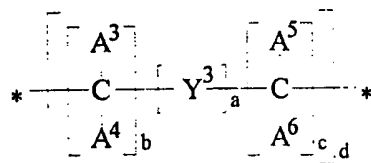
$Y^1$  and  $Y^2$  are independently selected from C, N, O, Si, P and S atoms;

$A^1$  and  $A^2$  are independently selected from hydrogen, alkyl, alkenyl and cycloalkyl (each of alkyl, alkenyl and cycloalkyl) being optionally substituted by one or more groups selected from hydroxy, aryl, heteroaryl, sulphonate, phosphate, electron

donating groups and electron withdrawing groups, and groups of formulae  $(G^1)(G^2)N-$ ,  $G^3OC(O)-$ ,  $G^3O-$  and  $G^3C(O)-$ , wherein each of  $G^1$ ,  $G^2$  and  $G^3$  is independently selected from hydrogen and alkyl, and electron donating and/or withdrawing groups (in addition to any amongst the foregoing);

5 i and j are selected from 0, 1 and 2 to complete the valency of the groups  $Y^1$  and  $Y^2$ ;

each of  $Q^1-Q^4$  is independently selected from groups of formula



10

wherein  $10 > a+b+c+d > 2$ ;

each  $Y^3$  is independently selected from  $-O-$ ,  $-S-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-(G^1)(G^2)N-$ ,  $-(G^1)N-$  (wherein  $G^1$  and  $G^2$  are as hereinbefore defined),  $-C(O)-$ , aryl, heteroaryl,  $-P-$  and  $-P(O)-$ ;

15 each of  $A^3-A^6$  is independently selected from the groups hereinbefore defined for  $A^1$  and  $A^2$ ; and

wherein any two or more of  $A^1-A^6$  together form a bridging group, provided that if  $A^1$  and  $A^2$  are linked without simultaneous linking also to any of  $A^3-A^6$ , then the bridging group linking  $A^1$  and  $A^2$  must contain at least one carbonyl group.

20

66. A dry textile having an organic substance as defined in any preceding claim applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02878

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 D06L3/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D06L C11D C07D C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 27772 A (PROCTER & GAMBLE) 19 October 1995 (1995-10-19) claims	1-66
A	WO 97 07124 A (RHONE POULENC CHEMICALS ;CARR JOHN FREDERICK (GB); PAKENHAM DEREK) 27 February 1997 (1997-02-27) claims	1-66
A	WO 96 06154 A (UNILEVER NV ;UNILEVER PLC (GB)) 29 February 1996 (1996-02-29) claims	1-66
P,A	DE 197 14 122 A (CLARIANT GMBH) 8 October 1998 (1998-10-08) the whole document	1-66

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

**\* Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 January 2000

Date of mailing of the international search report

14/01/2000

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02878

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 9707124 A	27-02-1997	GB 2310852 A EP 0785940 A US 5739367 A	10-09-1997 30-07-1997 14-04-1998
WO 9606154 A	29-02-1996	AU 3077495 A	14-03-1996
DE 19714122 A	08-10-1998	EP 0869171 A JP 11005993 A	07-10-1998 12-01-1999